VŠB – Technical University of Ostrava
Faculty of Safety Engineering
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&

Université Lille 1
UFR de physique
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DISSERTATION

to obtaine academic degree “doctor” in abbr. “Ph.D.”

Laboratory Spectroscopic Studies of reactive intermediates relevant to the combustion

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Ostrava, January 29th 2016

Declaration

„I hereby declare that the submitted dissertation is my own work and I affirm that all used sources of information have been indicated.“

In Ostrava 29. 1. 2016

Signature: .....

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Abstract

The goal of this thesis is to describe studies about molecular species invertigated by spectroscopic methods which are relevant to the safety sciences – it means first of all chemistry of combustion.

The first chapter called "Microwave spectroscopy of the $H_2{}^{12}C^{16}O$" deals with molecule of formaldehyde studied by microwave spectroscopic technique, namely rotational transitions within excited vibrational states in the millimeter-wave and submillimeter-wave region. This work has been motivated by the atmospheric and astrophysical importance of formaldehyde (H_2CO). The main aid of this study is to complete the already existing list of rotational transitions within the ground vibrational state by a list of transitions within the four first excited 2^1, 3^1, 4^1 and 6^1 vibrational states, to help the detections of this species by microwave or millimeterwave techniques.

In the second chapter called "Photoacoustic spectroscopy of the $C_7H_{14}O_2$" are interpretated absorption spectra of molecule of n-pethylacetate studied by photoacoustic detection (PAS) for concentration analysis. The absorption spectra of gaseous n-penthylacetate has been investigated by means of Fourier transform infrared spectroscopy (FTIR) as well as CO_2-laser photoacoustic spectroscopy (PAS) for simulation of the dispersion of a nerve agent (sarin) within a modeled atmospheric boundary layer. Three CO_2-laser emission lines has been used for photoacoustic detection of n-penthylacetate with detection limit in the range of 1-3 ppm.

And the last chapter called "Infrared spectroscopy of XCN^+" deals with molecular ions from CN• radical family, especially halogen-cyanide radical cations XCN^+ (X = Br, I, Cl) studied by use of tunable diode-laser (TDL) infrared spectroscopic technique. Radical cation ICN^+ has been studied theoretically and also experimentally by means of this method as well as by means of the FTIR spectroscopy in the discharge plasma as a simulation of exothermic medium. Series of the lines with periodic wavenumber distances have been detected. It is supposed that they indicate new generated species that has been proved by Loomis Wood analysis. Furthermore the FTIR spectra have been recorded and individual bands have been assigned to determinate the chemical composition of the newly generated species at discharge conditions.

Keywords: safety sciences, spectroscopy, combustion chemistry

Abstrakt

Cílem této disertace je characteritika molekulárních iontů významných z hlediska bepečnostních věd, což znamená především chemie hoření, vyšetřovaných pomocí vybraných spektroskopických metod.

První kapitola nazvaná “Microwave spectroscopy of the $H_2{}^{12}C^{16}O$” se zabývá mikrovlnnými spektry molekuly formaldehydu, přesněji rotačními přechody v rámci excitovaných vibračních stavů v milimetrové a submilimetrové oblasti elektromagnetického spectra. Tato studie byla motivována atmosférickou a astrofyzikální důležitostí formaldehydu (H_2CO) a jejím hlavním cílem bylo doplnění již existujícího přehledu rotačních přechodů v rámci základního vibračního stavu molekuly o zcela nový soupis přechodů v rámci čtyř prvních excitovaných vibračních stavů 2^1, 3^1, 4^1 a 6^1 k zlepšení detekce této spécie pomocí metod mikrovlnné či milimetrové spektroskopie.

Ve druhé kapitole nazvané “Photoacoustic spectroscopy of the $C_7H_{14}O_2$” jsou interpretována apbsorpční spectra molekuly n-pentylacetátu zkoumaná metodou optoakustické spektroskopické detekce (PAS) ke koncentrační analýze. Absorpční spektra plynného n-pentylacetátu byla zkoumána infračervenou spektroskopií s Fourierovou transformací (FTIR) a zároveň CO_2-laser optoakustickou spektroskopií (PAS) k přímé kvantitativní spektroskopické detekci stopových množství plynu a následné využití této metody při experimentech fyzikálních simulací šíření zástupce nervového plynu (sarinu) uvnitř modelované mezní vrstvy atmosféry v nízkorychlostním aerodynamickém tunelu.

A poslední kapitola nazvaná “Infrared spectroscopy of XCN^+” se zabývá studiem molekulárních iontů z řady CN• radikálů, především halogen-kyanidových radikálových kationtů XCN^+ (X = Br, I, Cl) s použitím metod laditelné laser-diodové (TDL) infračervené spektroskopie. Radikálový kation ICN^+ byl studován teoreticky a experimentálně pomocí této metody, stejně tak pomocí FTIR spektroskopie, v nízkoteplotním výbojovém plazmatu jako simulace exotermického prostředí. Byla detekována řada linií s pravidelným vlnočtovým rozestupem, které pravděpodobně indikují nové spécie vznikající ve výboji, což bylo prověřeno analýzou v programu LoomisWood. Dále byla zaznamenána FTIR spektra a byly přiřazeny jednotlivé pásy k přesnějšímu určení chemického složení nově generovaných spécií ve výbojových podmínkách.

Klíčová slova: bezpečnostní vědy, spektroskopie, chemie hoření

Summary

The title of presented work **"Laboratory spectroscopic studies of reactive intermediates re levant to the combustion"** describes its motif as well. It is complex of studies using spectroscopic methods to measure diverse species under the laboratory conditions. The species which are somehow interesting from the combustion and burnig proceses point of view together with the processes producing toxic species. The assortment of studied molecules in gas phase represents intermediates and terminal products of mentioned processes that can be both reactive or stable particles, they are further more relevant from the point of view of combustion chemistry, atmospherical chemistry and last but not least astrochemistry. The text itself is topically devided to the three chapters according to every individual study.

The first chapter called **"Microwave spectroscopy of the $H_2{}^{12}C^{16}O$"** deals with molecule of formaldehyde studied by microwave spectroscopic technique, namely rotational transitions within excited vibrational states in the millimeter-wave and submillimeter-wave region. This work has been motivated by the atmospheric and astrophysical importance of formaldehyde (H_2CO). The main goal of this study has been to complete the already existing list of rotational transitions within the ground vibrational state by a list of transitions within the four first excited 2^1, 3^1, 4^1 and 6^1 vibrational states, to help the detections of this species by microwave or millimeterwave techniques. For this purpose, the rotational spectra of H_2CO in the 2^1, 3^1, 4^1 and 6^1 excited vibrational states have been investigated in Lille and Cologne in the millimeter region at 160 – 600 GHz and 850 – 903, respectively. The results of these measurements has been than combined with the 2^1, 3^1, 4^1 and 6^1 infrared energy levels, which has been obtained from previous analysis of FTS spectra of the

ν_4, ν_6 and ν_3 bands recorded in 10 μm region and more recently for the ν_2 fundamental band. The energy level calculation of the 2^1, 3^1, 4^1 and 6^1 interacting states accounts for the various Coriolis-type resonances that perturb the energy levels of the 2^1, 3^1, 4^1 and 6^1 vibrational states as well as for the anharmonic resonances coupling the 2^1 and 3^1 energy levels, and in this way the microwave and infrared data could be reproduced within their associated experimental uncertainty. However, it is clear that the theoretical model used to account for the very large A-type Coriolis resonance linking the 4^1 and 6^1 energy levels of H_2CO is only effective with poor physical meaning. This study has been solved and also partially treated in the Laboratory of laser, atom and molecular physics, at the University of Sciences and Technologies Lille 1 in France within international project QUASAAR (Quantitative Analysis for Atmospheric and Astrophysical Research) under the leading of prof. Georgés Wlodarczak and Dr. Laurent Margulés, where my research work has been performed within the study so-called „doctorat en co-tutelle“ – „doctorate under joint supervision“.

In the second chapter called **“Photoacoustic spectroscopy of the $C_7H_{14}O_2$”** are interpretated absorption spectra of molecule of n-pethylacetate studied by photoacoustic detection (PAS) for concentration analysis. Gaseous n-pentylacetate (n-amylacetate) has been recently employed in dispersion studies instead of sarin ($C_4H_{10}FO_2P$). An extremely toxic nerve agent is represented by a non-toxic tracer with similar physical – chemical characteristics such as vapor pressure, boiling point or molecular mass. The absorption spectra of gaseous n-penthylacetate has been investigated by means of Fourier transform infrared spectroscopy (FTIR) as well as CO_2-laser photoacoustic spectroscopy (PAS) for simulation of the dispersion of a nerve agent (sarin) within a modeled atmospheric boundary

layer. An FTIR spectra has been recorded by the Bruker IFS 120 spectrometer within a range of 600 – 2000 cm^{-1} comfirmed the absorption maximum around 1240 cm^{-1} corresponding to the C-O stretch. The spectral region available for PAS detection (9-11μm) is characterized by a broad and weak absorption band of n-pentylacetate. Three CO_2-laser emission lines has been used for photoacoustic detection of n-penthylacetate with detection limit in the range of 1-3 ppm. These concentration levels are expected in wind tunnel modeling dispersion experiment. A generation of trace amounts of n-pentylacetate has been obtained by the use of precise concentration standards based on the permeation method, standards were made of polyethylene and Teflon tubes. Based on all available information the CO_2-laser photoacoustic spectrum of gaseous n-pentylacetate has been recorded for the first time. This study has been solved partialy at the Faculty of Safety Engineering, VŠB – Technical University of Ostrava and partialy at the dispersal compartment of Institute of Thermomechanisc in Nový Knín under the scientific leading of prof. Ing. Zdeněk Zelinger, CSc.

And the last chapter called “Infrared spectroscopy of XCN^+” deals with molecular ions from CN• radical family, especially halogen-cyanide radical cations XCN^+ (X = Br, I, Cl) studied by use of tunable diode-laser (TDL) infrared spectroscopic technique. Radical cation ICN^+ has been studied theoretically and also experimentally by means of this method as well as by means of the FTIR spectroscopy in the discharge plasma as a simulation of exothermic medium. The molecular ions are important species from the point of view of its existence and they are considerable subject of research in the field of chemistry, physics and astronomy. The tunable diode laser (TDL) infrared spectroscopy has been proved as a sufficiently effective and sensitive for the detection of free radicals and molecular ions. The intimate study of

the fundamental band of BrCN+ molecule has been performed by means of this method in infrared region. However, the corresponding studies of ICN+ and ClCN+ have not been done up to the present time. The spectroscopic constants of mentioned radical ions are unknown or partially known, and therefore we onward proposed spectroscopic searching of rotational-vibrational transitions of these ions. The knowledge of the infrared spectra of studied ions is a necessary precondition for subsequent research in the range of microwave spectroscopy. The TDL absorption infrared spectroscopic method has been applied for the open study of radical cation ICN+ in the region about 2080 cm-1, which is corresponding to middle of the band according to the previous studies. This experiment has been supplemented by the high resolution Fourier transform infrared (FTIR) spectroscopy. Since the TDL infrared spectroscopy provides sensitivity and the FTIR spectroscopy provides broad spectral range, these methods have been selected for investigation of combustion and burning processes including production of reactive intermediates and terminal products. The both of these explorations have been performed in the discharge plasma to simulate an exothermic medium. The hollow cathode discharge has been used in case of TDL spectroscopy. Series of the lines with periodic wavenumber distances have been detected. It is supposed that they indicate new generated species that has been proved by Loomis Wood analysis. Furthermore the FTIR spectra have been recorded and individual bands have been assigned to determinate the chemical composition of the newly generated species at discharge conditions. The microwave discharge has been used for the experiment by FTIR spectrometer. This study has been performed under the scientific leading of prof. Ing. Zdeněk Zelinger,CSc. at the nursery of Heyrovsky Institute of Physical chemistry of CAS,

which has an agreement about collaboration with the Faculty of Safety Engineering, VŠB – Technical University of Ostrava.

All the experimental as well as theoretical backgrounds of dissertation have been solved and treated within internation collaboration in between Faculty of Safety Engineering, VŠB – Technical University of Ostrava and Laboratory of lasers, atoms and molecular physics, University of Sciences and Technologies Lille 1 in France. This collaboration is great contribution for the subject field “Fire protection and industrial safety” not only due to availability of modern spectroscopic technics.

Souhrn

Název předkládané práce **“Laboratory spectroscopic studies of reactive intermediates relevant to the combustion”** vystihuje také její téma. Jedná se o soubor studií využívajících spektroskopických metod k měření rozličných spécií v laboratorních podmínkách zajímavých z hlediska hoření a procesů hoření společně s procesy produkujícími toxické spécie. Vybrané studované molekuly v plynném skupenství jsou meziprodukty a konečné produkty zmiňovaných procesů, které mohou být reaktivními i stabilními částicemi a jsou dále významné také z hlediska chemie hoření, atmosférické chemie a v neposlední řadě i astrochemie. Samotný text je tématicky rozdělen do tří kapitol podle jednotlivých studií.

První kapitola nazvaná **“Microwave spectroscopy of the $H_2{}^{12}C^{16}O$”** se zabývá mikrovlnnými spektry molekuly formaldehydu, přesněji rotačními přechody v rámci excitovaných vibračních stavů v milimetrové a submilimetrové oblasti elektromagnetického spektra. Tato studie byla motivována atmosférickou a astrofyzikální důležitostí formaldehydu (H_2CO) a jejím hlavním cílem bylo doplnění již existujícího přehledu rotačních přechodů v rámci základního vibračního stavu molekuly o zcela nový soupis přechodů v rámci čtyř prvních excitovaných vibračních stavů 2^1, 3^1, 4^1 a 6^1 k zlepšení detekce této spécie pomocí metod mikrovlnné či milimetrové spektroskopie. Rotační spektra H_2CO v 2^1, 3^1, 4^1 a 6^1 excitovaném vibračním stavu byla pro tento účel zkoumána v Lille a Kolíně v oblasti 160-600 GHz a 850-903 GHz v tomtéž pořadí. Výsledky těchto měření byly poté zkombinovány s 2^1, 3^1, 4^1 a 6^1 infračervenými energetickými hladinami, jenž byly získány z předchozí analýzy FTS spekter pásů ν_4, ν_6 a ν_3 zaznamenaných v 10 μm oblasti, a před nedávnem také ze základního pásu ν_2. Výpočty pro 2^1, 3^1, 4^1 a 6^1

interagující stavy jsou sestaveny pro různé typy Coriolisových rezonancí, jež narušují energetické hladiny těchto vibračních stavů, a rovněž pro anharmonickou rezonanci spojující 2^1 a 3^1 energetickou hladinu, a tímto způsobem mohou být mikrovlnná a infračervená data reprodukována v rámci jejich přiřazené experimentální nejistoty. Avšak je zřejmé, že teoretický model uvažovaný pro velmi silný A-typ Coriolisovy rezonance svazující 4^1 a 6^1 energetickou hladinu H_2CO je účinný jedině s nízkým fyzikálním významem. Tato studie byla řešena a částečně i zpracovávána v Laboratoři laserové atomové a molekulové fyziky, University věd a technologií Lille 1 ve Francii v rámci mezinárodního projektu QUASAAR (Quantitative Analysis for Atmospheric and Astrophysical Research) pod odborným vedením prof. Georgese Wlodarczaka and Dr. Laurenta Margulése, kde probíhala má výzkumná činnost v rámci tzv. studia „doctorat en co-tutelle“ - „doktorát pod dvojím vedením“.

Ve druhé kapitole nazvané **Photoacoustic spectroscopy of the $C_7H_{14}O_2$** jsou interpretována apbsorpční spectra molekuly n-pentylacetátu zkoumaná metodou optoakustické spektroskopické detekce (PAS) ke koncentrační analýze. Plynný n-pentylacetát (n-amylacetát) byl v minulosti a také v nedávné době použit při rozptylových studiích namísto sarinu ($C_4H_{10}FO_2P$). Extrémně toxická látka, jejíž samotné využití je jako nervový plyn byla reprezentována jejím netoxickým zástupcem s podobnými fyzikálně-chemickými vlastnostmi, jako je například tlak par, bod varu nebo molekulová hmotnost. Absorpční spektra plynného n-pentylacetátu byla zkoumána infračervenou spektroskopií s Fourierovou transformací (FTIR) a zároveň CO_2-laser optoakustickou spektroskopií (PAS) k přímé kvantitativní spektroskopické detekci stopových množství plynu a následné využití této metody při experimentech fyzikálních simulací šíření zástupce nervového plynu (sarinu) uvnitř

modelované mezní vrstvy atmosféry v nízkorychlostním aerodynamickém tunelu. FTIR spektra byla zaznamenána komerčně dostupným Bruker IFS 120 spektrometrem v oblasti 600-200 cm^{-1} potvrzující absorpční maximum okolo 1240 cm^{-1} odpovídající C-O stretch pásu. Ačkoli spektrální oblast dostupná pro PAS (9-11μm) je charakterizována širším a mnohem slabším absorpčním pásem n-pentylacetátu, k optoakustické detekci plynného n-pentylacetátu byly použity tři emisní linie CO_2-laseru s detekčním limitem v rozsahu 1-3 ppm, které byly vyhodnoceny jako vhodné dosáhnout detekčního limitu v řádu jednotek ppm, což odpovídá přepokládané koncentraci dosažitelné ve větrném tunelu. Produkci sledovaného množství n-pentylacetátu (10-500 ppm) zajišťovaly přesně stanovené permeační standardy vyrobeny z polyetylenu a Teflonu založené na principu permeace. Na základě dostupných informací CO_2-laser optoakustické spektrum plynného n-pentylacetátu bylo zaznamenána poprvé. Tato studie byla řešena z části na Fakultě bezpečnostního inženýrství VŠB – Technické university Ostrava a z části na detašovaném pracovišti Ústavu termomechaniky AV ČR, v Laboratoři aerodynamiky životního prostředí v Novém Kníně pod odborným vedením pana prof. Ing. Zdeňka Zelingera, CSc.

Poslední kapitola nazvaná **"Infrared spectroscopy of XCN^+"** se zabývá studiem molekulárních iontů z řady CN• radikálů, především halogen-kyanidových radikálových kationtů XCN^+ (X = Br, I, Cl) s použitím metod infračervené spektroskopie. Molekulární ionty jsou z hlediska jejich výskytu významným objektem bádání v oblastech chemie, fyziky a astronomie. Vysoce rozlišená laditelná laser-diodová infračervená spektroskopie (TDL) se osvědčila jako efektivní a citlivá metoda pro detekci volných radikálů a molekulárních iontů, a s jejím použitím byla provedena první studie základního pásu $BrCN^+$ v infračervené oblasti, avšak nebyly provedeny odpovídající studie pro ICN^+ a $ClCN^+$ ionty.

Spektroskopické konstanty zmíněných radikálových iontů jsou známy jen částečně nebo vůbec, a proto jsme navrhli spektroskopické hledání jejich rotačně-vibračních přechodů. Získání infračervených spekter studovaných iontů by bylo velkým přínosem pro následné unikátní měření v oblasti mikrovlnné spektroskopie. TDL infračervená spektroskopie společně s vysoce rozlišnou infračervenou spektroskopií s Fourierovou transformací (FTIR) byly vybrány k výzkumu hoření a spalovacích procesů zahrnujících produkci reaktivních meziproduktů a konečných produktů. TDL spekroskopie poskytuje vysokou citlivost a FTIR spektroskopie zajišťuje široký spektrální rozsah studovaných procesů. Radikálový kation ICN^+ byl studován teoreticky a experimentálně pomocí těchto metod v nízkoteplotním výbojovém plazmatu jako simulace exotermického prostředí. Pro experiment prováděný pomocí TDL spektroskopie byl použit výboj z duté katody a měření byla prováděná v oblasti kolem 2080 cm^{-1}, což podle předchozích studií odpovídá středu pásu. Pomocí této metody byla detekována řada linií s pravidelným vlnočtovým rozestupem, které pravděpodobně indikují nové spécie vznikající ve výboji, což bylo prověřeno analýzou v programu LoomisWood. Dále byla zaznamenána FTIR spektra a byly přiřazeny jednotlivé pásy k přesnějšímu určení chemického složení nově generovaných spécií ve výbojových podmínkách. Pro experiment prováděný pomocí FTIR spektrometru byl použit mikrovlnný výboj. Tato studie byla řešena převážně na školícím pracovišti Ústavu fyzikální chemie J. Heyrovského AV ČR, které je provázáno smlouvou o spolupráci s Fakultou bezpečnostního inženýrství VŠB – Technické university Ostrava, pod odborným vedením prof. Ing. Zdeňka Zelingera, CSc.

Veškeré experimentální, ale i teoretické podklady práce byly řešeny a zpracovávány v rámci mezinárodní spolupráce mezi Fakultou bezpečnostního inženýrství VŠB – Technické univerzity

Ostrava, Ústavu fyzikální chemie J. Heyrovského AV ČR a Laboratoře laserové atomové a molekulové fyziky, University věd a technologií Lille 1 ve Francii. Tato spolupráce je velkým přínosem pro obor „Požární ochrana a bezpečnost průmyslu“ nejen z hlediska dostupnosti moderních spektroskopických technik.

Goals of the thesis

A formulation of particular studies concerning present work is listed below:

- ✓ Realization of a bibliographic search concerning theoretical computations and experimental measurements of rotational transitions of the ground vibrational state of formaldehyde molecule H_2CO and its isotopomers (e.g. $H_2{}^{13}C^{16}O$ and $H_2{}^{12}C^{18}O$) in the gas phase.
- ✓ Implementation of the methodology for spectral measurements using the molecules of CH_3CCl_3 and $HCOOCH_2D$ as examples by means of a microwave spectrometer. Description of the experimental setup, its individual parts, their corresponding functions and basic operational principles. Subsequent description of optimization of conditions for production and detection of H_2CO in the gas phase.
- ✓ Based on the prediction of rotational frequencies (obtained by means of *ab initio* calculations of molecular constants within the scope of other theoretical studies) perform a measurement using the Lille MMW spectrometer in millimeter and submillimeter range (150-660 GHz). First in the ground vibrational state for the sake of experimental optimization and subsequently in the first excited vibrational state.
- ✓ Evaluate the experimental data in order to obtain the values of rotational frequencies of the highly resolved spectral lines of H_2CO in the gas phase. Describe the potential applications of the results within the field of molecular spectrometry and astrophysics and within the context of fire protection and industrial safety management.
- ✓ Carry-out of the bibliographic search concerning the means of exploitation of the method of photoacoustic detection in the field of safety engineering - particularly its use for monitoring of

dangerous chemical substances in gaseous phase. Cary-out of the publication searchconcerning similarities between the model molecule of n-penthylacetate and the molecule of Sarine.

- ✓ Scan of the entire spectral range of the n-penthylacetate by means of the FT IR. Build-up and tuning of the laser photoacoustic experimental setup, preparation of the concentration standards of the model gas n-Pentylacetate and final measurement of concentrations using selected emission lines of the CO_2-laser.
- ✓ Evaluation of the experimental results, calculating of the detection limit and the quantification limit of the analyzer. Description of potential applications of the obtained results and their implementation in simulation of the spread of one representative of the neurotoxic gas family (Sarine) within simulated boundary layer of the atmosphere.
- ✓ Realization of publication search on the topic of molecular ions, above all cations - the unstable radical species that play significant role in the environments of flames and physical plasmas - by means of various spectroscopic techniques. Study of XCN^+ (X = Br, I, Cl) radical cations, members of the group of CN• radical ions.
- ✓ Set-up and optimization of the laser-diode spectrometer, description of the involved experimental arrangement. Study of the radical cation $BrCN^+$, which was not carried out with enough detail in the IR range in the past. Calibration of the experimental apparatus using the known lines of the $BrCN^+$.
- ✓ Search for further lines of significant unstable species in the IR spectrum, e.g. those of CN• radical and $BrCN^+$ ion. Consecutive search for up-to-now not-measured spectral lines of radical cations ICN^+ a $ClCN^+$. Preparation and test of precursors.

Methodology of the thesis

Several spectroscopic methods were used to aid in reaching the goals of this work. The methods, in order of nominal appearance of corresponding studies in the section Summary - are listed below:

1. Microwave and millimeter spectroscopy,
2. CO_2-laser photoacoustic spectroscopy (PAS)
3. Laser-diode absorption spectroscopy.

These methods are described in greater detail in the same order in sections 5, 10 and 16.

Results of the thesis

Partial results of the individual studies contained within the scope of this work are listed in the list of publication and desctribed individualy in sections 6, 11 and 17.

Contents

List of figures and tables

1. General Introduction

The high resolution molecular spectroscopy (HRMS) is a relatively young and thus modern scientific branch of knowledge that is closely related to the natural sciences and consequently also to the branches of fire protection and industrial safety. The spectroscopy, apart from other things, strongly contributes to the development of all these branches that come under the safety engineering disciplines. Since the experimental molecular spectroscopy together with the theory provide us the information about the molecular structure, the development in many other scientific branches such as, for example, atmospheric chemistry and astrochemistry is based on results of the molecular spectroscopy. With respect to objectives and orientation of the Department of Fire Protection it is, first of all, chemistry of combustion, studies of the processes in the flames, or also monitoring of dangerous chemical matters in the gas phase, where the spectroscopy can significantly contribute with the help of modern experimental techniques.

One of the fundamental and still open tasks of Safety Engineering is characterization of physical-chemical effects related to the combustion, procecesses of matter burning and processes producing toxic species. The characteristic properties of flame burning of matter are connected with chemical composition in the relevant process as, for example, chemical composition of the flames. The components of such processes are as well intermediates (e. g. ions in plasma) and terminal products (e. g. product of combustion as the atmospheric pollution) of combustion. Toxic intermediates of combustion can be both reactive and stable particles. The essential role in the processes, that are asserted in flame burning of matter and their extinguishing, play reactive unstable particles, in the first place

radicals and in many cases also ions, as well as stable particles in a combustion product form. These particles are further related to the contaminated atmosphere by trace amount of manifold gaseous pollutants that has subsequently also huge inpact on the environment. It is possible to clarify these phenomena of the individual burning and extinguishing processes with the aid of laboratory experiments, where one can study isolated elementary reactions with the possibility of spectroscopic monitoring.

Nowadays, physical methods primarily based on spectroscopic methods are very often applied for detection of the molecules in gas phase. The study and measurement of the absorption, emission or scattering of the electromagnetic radiation by matter as a function of the wavelength, wave nubmer or frequency of the radiation, is the subject of spectroscopy. On the basis of the fact that each atom and molecule has the unique spectrum, the spectroscopy is the most important source of information about the composition of the matter and also the atomic or molecular properties that has broad range of application in all fields of chemical research – qualitative and quantitative analysis. The complete knowledge of the spectral characteristics is necessary precondition for monitoring, which is often exploited of late in the safety engineering, for example, in the study of dangerous chemical species in the gas phase formation and the like. Spectroscopic methods are suitable for the concentration analysis of the gas phase composition under laboratory conditions as well as for direct detection in the free atmosphere. This is very important for the risk estimation and for the security and safety research, among others even for the prevention of environmental disasters.

The practical application of the spectroscopic methods to study of radicals and ions then require high sensitivity and resolution. The high sensitivity is important for the reason of short

life times and relatively low concentrations of radicals and ions, and high resolution enables unambiguous identification of individual species, i. e. selectively distinguish lines of different radicals and lines of mother molecules.

The spectroscopic measurements are carried out in all regions of the electromagnetic radiation, i. e. from radio waves to gamma rays. The following chapters are focused on the molecular absorption spectroscopy of gaseous samples in the millimeter-wave, submillimeter-wave and infrared region, in the area where the pure rotational, rotational-vibrational and vibrational transitions are observed and studied.

The fundamental principles of the spectroscopic experiment are described in tens of monograps [1-3] and the graphical demonstration is pictured on **Figure 1-1** bellow.

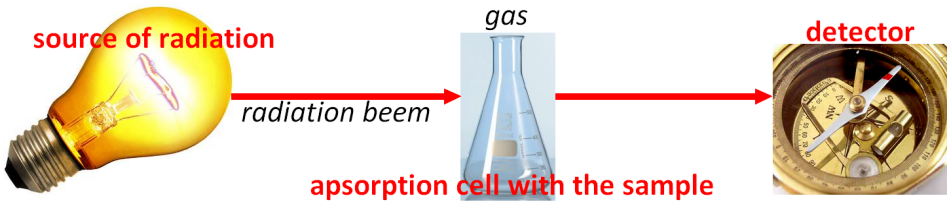

Figure 1-1: *Typical demonstration of spectroscopic experiment with source of radiation, absorption cell with the sample and detector. The example of electromagnetic radiation absorption after passing through the studied gas phase molecular sample as a function of frequency (wave length, wave number, photon energy etc.).*

CHAPTER I

MICROWAVE SPECTROSCOPY OF THE H_2CO

Rotational transitions of the molecule of formaldehyde – $H_2{}^{12}C^{16}O$ – within the four first excited vibrational states

2. Introduction to Chapter I

This chapter deals with the molecule of formaldehyde studied by microwave spectroscopic technique, namely rotational transitions within excited vibrational states in the millimeter-wave and submillimeter-wave region.

This work has been motivated by the atmospheric and astrophysical importance of formaldehyde (H_2CO) – see section 3. The main goal of this study has been to complete the already existing list of rotational transitions within the ground vibrational state by a list of transitions within the four first excited 2^1, 3^1, 4^1 and 6^1 vibrational states, to help the detections of this species by microwave or millimeterwave techniques. For this purpose, the rotational spectra of H_2CO in the 2^1, 3^1, 4^1 and 6^1 excited vibrational states have been investigated in the millimeter region at 160 – 600 GHz.

This study has been solved and also partially treated in the laboratory of the Lille 1 University in France within the international project scholarship QUASAAR under the leading of prof. Georgés Wlodarczak and Dr. Laurent Margulés. In this study I have participated mainly the experimental part.

2.1. Microwave spectroscopy

Molecular spectra have previously been well described from the point of view of infrared spectroscopy *(Chapter III.)* – but the different frequency range, higher resolution, and greater accuracy of microwave spectroscopy makes available for study rather different types of phenomena such as for example hyperfine structure, pressure broadening, and Stark or Zeeman effects.

High-resolution rotational spectroscopy is a technique that is used mainly to detect molecules in the gas phase. It is a unique method based on the foundations of quantum mechanics. The study of the interaction of microwave and submillimeter electromagnetic radiation with the molecular environment delivers a detailed knowledge of the spectral, chemical and quantum mechanical properties of molecules and molecular fragments. Thanks to a very sophisticated theory of microwave spectroscopy, these findings may be analyzed and simulated in order to obtain key spectroscopic information necessary for the interpretation of atmospheric and astrophysical measurements. Detailed characterization of the molecular structure of the model substance also contributes to the explanation of the phenomena in chemical reactions and, of course, the processes of combustion or fire suppression. Specific spectroscopic characteristics obtained by studying the rotational transitions of molecules on this model allows to continue the study of molecules of a similar type. The object of rotational spectroscopy is the study of spectroscopic transitions between quantum states of molecules that differ only by the rotational quantum numbers, i.e. spectroscopic transitions, during which there is no change in vibrational or electronic state, mainly within the limits of the basic vibrational and basic electronic states. In this study, however, we also deal with rotational transitions within the first excited vibrational states.

When measuring the rotational structure of the energy levels of the examined molecule, its rotational movement must be sufficiently free; therefore, we can speak mainly about the spectroscopy of gases or substances that can convert into a gas phase. The energy differences between the different rotational states are usually significantly less than those between the different vibrational or even electronic states. While the electron spectra are usually observable in the visible and ultraviolet regions

(UV, VIS) and the vibrational spectra in the infrared region (IR), the differences between the rotational levels usually correspond to the so-called “microwave” region of the spectrum (MW). This area is situated between the infrared and radio frequency areas, i.e., in the field of frequencies from 300 MHz up to hundreds of gigahertz (GHz), as shown in the (**Figure 2-1**). The interval expressed in wavelengths has a range from tenths of a millimeter to tens of centimeters.

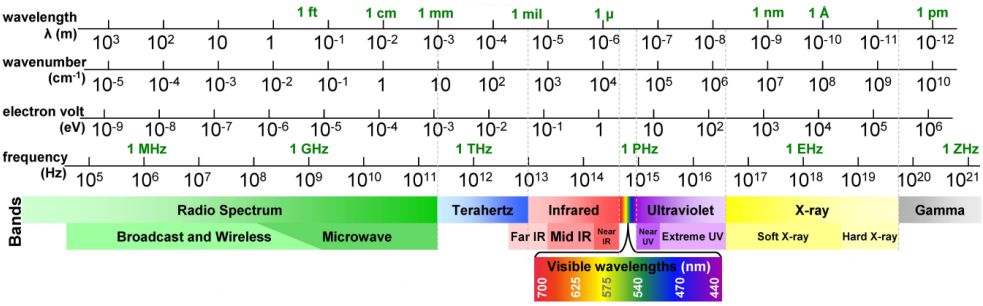

Figure 2-1: *The electromagnetic spectrum classified according to the radiation wavelengths, wavenumbers, electron volts and frequencies.*

The spectrum obtained during the experiments in the microwave region of the electromagnetic radiation is a graphical representation of the detected intensity of energy in relation to the energy frequency. In microwave spectroscopy, the most commonly used unit is Hertz (see section 5). However, often it may be useful to know the relations between various units used by other spectroscopies in different regions of electromagnetic radiation (**Figure 2-1**).

Unit	cm^{-1}	MHz	kJ	eV	$kJ\ mol^{-1}$
$1\ cm^{-1}$	1	29 979.25	$1.986\,447\times10^{-26}$	$1.239\,842\times10^{-4}$	$11.962\,66\times10^{-3}$
1 MHz	$3.335\,64\times10^{-5}$	1	$6.626\,076\times10^{-31}$	$4.135\,669\times10^{-9}$	$3.990\,313\times10^{-7}$
1 kJ	$5.034\,11\times10^{25}$	$1.509\,189\times10^{30}$	1	$6.241\,506\times10^{21}$	$6.022\,137\times10^{23}$
1 eV	8065.54	$2.417\,988\times10^{8}$	$1.602\,177\times10^{-22}$	1	96.485 3
$1\ kJ\ mol^{-1}$	83.593 5	$2.506\,069\times10^{6}$	$1.660\,540\times10^{-24}$	$1.036\,427\times10^{-2}$	1

Figure 2-2: *The useful conversion factors.*

An important feature of microwave spectroscopy is that the intensity of the purely rotational microwave transitions, compared to the rovibrational and rovibronic transitions in the infrared, visible and ultraviolet regions of the spectrum, is significantly lower. The reasons for this are not the small matrix elements of the transition moment but the fact that the difference in population of rotational states is relatively small. The intensity of the absorption transitions between two states with energies of E_l (state of lower energy) and E_u (state of higher energy) are directly proportional to the difference of the populations in both states N_l - N_u:

eq. 2-1:

$$N_l - N_u = N \times (F_l - F_u) = N \times \{exp[-E_l/kT] - exp[-E_u/kT]\}/$$
$$Q_{int}(T) = N \times exp[-E_l/kT]\{1 - exp[-h\nu_{ul}/kT]\}/Q_{int}(T)$$

where N is the total number of molecules, F_l and F_u are fractions of the lower and higher (energy-richer and poorer) states. It is obvious that if the energy states E_l and E_u are close, which is the case of microwave transitions, the difference in population of rotational states is very low. From the equation (eq. 2-1:) follows that, for example, for a typical infrared transition from basic state at 2000 cm^{-1}, the difference of fractions F_l - F_u is more than 60 times greater than for a similar transition (with the same matrix element of the dipole moment and from the same level) at 100 GHz and more than 220 times greater than the analogous transition at 30GHz. Absorption coefficients in the microwave area are therefore very low. Since, according to the Lambert-Bouguer law (eq. 2-2:), a direct proportion applies between the radiation entering the molecular absorption environment I_0 and the radiation ***I*** leaving the system:

eq. 2-2:

$$I = I_0 \exp(-k \times l)$$

where *l* is the length of the absorption environment and *k* is its specific value of absorption (the linear absorption coefficient), it is possible to achieve higher response to the detector using the incoming radiation of higher performance, but with the risk of saturation of the transition due to the small difference in the Boltzmann population of energy levels. A more graceful solution is to extend the absorption track.

The advantage of spectroscopy in this frequency range is the Doppler broadening of spectral lines, which is approximately three orders lower than for the infrared area. Assuming that the pressure (collision) line broadening is suppressed, each line "occupies" a very narrow part of the overall spectrometer range, which is further reflected in its generally high resolution and eliminates the possibility of overlapping of two or more lines. A substantial advantage of microwave spectroscopy is its extraordinary accuracy of measurement thanks to the high monochromaticity and stability of microwave radiation source frequency, which enables to bind the experiment directly to a time (frequency) standard. No other type of spectroscopy, with the exception of hybrid techniques such as *sideband* spectroscopy [4, 5] or laser saturation spectroscopy [6, 7] provides such precision. Direct theoretical dependency of rotational spectroscopic parameters on the molecular geometry is also important for structural analysis.

The aim of this paper is not to describe in detail all aspects of the theory of rotational spectra; therefore, the following section provides only the basis needed for the subsequent interpretation of the experimental data. Those interested in a more detailed study may find the necessary information in the world technical

literature that offers a comprehensive range of excellent textbooks and monographs [8-11].

All of the mentioned monographs make reference to the principal book about rotational and microwave spectroscopy written by famous couple C. H. Townes and A. L. Schawlow (The Nobel Price Laureates). This book is already more than half of the century old but its corrected Dover etidion serves as a bible of rotational spectroscopy in every „microwave“ laboratory (C. H. Townes and A. L. Schawlow, „Microwave Spectroscopy“, Dover Publications, Inc., New York 1975).

3. Motivation and previous studies

Formaldehyde is one of the most extensively studied molecules that play important role in the atmospheric chemistry, chemistry of combustions, photochemistry of the troposphere etc. – there are many reasons for its interest. One of the goals of present study is to have a more complete description of the millimeter-wave and submillimeter-wave spectrum in the excited vibrational states for possible astrophysical applications.

Formaldehyde (methanal) is the chemical compound with the formula H_2CO. The simplest aldehyde, that was synthesized by the Russian chemist Aleksandr Butlerov for the first time, but it was conclusively identified by August Wilhelm von Hofmann. Formaldehyde exists several forms acide from H_2CO: the cyclic trimer trioxane and the polymer paraformaldehyde. Additionally it exists as the hydrate $H_2C(OH)_2$ in water.

The reliable prediction of rotational spectra of formaldehyde is important from several points of view, for example, from atmospheric, astrophysical and spectroscopic poit of view:

3.1. Atmospheric interest

From the atmospheric point of view, the formaldehyde is an intermediate of the oxidation or combustion of methane as well as other carbon compounds. It can be found in the smoke from forest fires, in the automobile exhaust, and in the tabacco smoke. In the atmosphere, formaldehyde is produced by the action of sunlight and oxygen on atmospheric methene and other hydocarbons. It thus becomes part of smog pollution. It is an important atmospheric pollutant – even in indoor environment – there is a relevant concentration of formaldehyde in urban air (indicator of

pollution in industrial cities). Small amounts of formaldehyde are produced as a metabolic product in most of the organisms including humans. The formaldehyde has a huge impact on environment and human health as one of the toxic intermediates of combustion.

3.2. Astrophysical interest

From the astrophysical point of view, the formaldehyde is one of the most abundant and one of the first polyatomic molecules detected in interstellar clouds (at first in 1968) and it was indentified in several cometary objects mostly at millimeter wavelengths – all of the formaldehyde isotopic species has been detected (e. g. it was observed in Orion molecular clouds or low-luminosity protostar Iras). The molecule of formaldehyde is also associated with theories about the origin of life on the Earth.

3.3. Spectroscopic interest

From the spectroscopic point of view it is then necessary to have accurate experimental data to verify the accuracy of *ab initio* calculation. The molecule of formaldehyde consists of four atoms and thus it is relatively small light tetraatomic molecule with the large rotational constants and relatively large dipole moment (μ=2,3D). Therefore it also has a strong submillimeter spectrum. It is possible to verify convergency of Watson Hamiltonian thanks to this model molecule. The formaldehyde is hence the key to our understanding of spectroscopy of polyatomic molecules – the model approximates a description of reality.

3.4. Properties

This substance is a flamable, colorless gas with a pungent, suffocating odor. Although formaldehyde is a gas at room temperature, it is readily highly soluble in water (up to 55%), acetone, benzene, chloroform, diethyl ether, and ethanol. The gas is stable in the absence of water, but it is incompatible with oxidizers, alkalis, acids, phenols, and urea. Explosive reactions occur with peroxide, nitrogen oxide, and performic acid. Anhydrous gaseous formaldehyde is not available commercially. Most formaldehyde is sold as a saturated aqueous solutios, known as formalin or formol, containing 30% to 50% formaldehyde with 0.5% to 15% methanol as a polymerization inhibitor. Polymerization may also be inhibited by the addition of up to 100 mg/kg of stabilizers such as cellulose ethers (IARC 1982, 1995, ATSCD 1999). In water, formaldehyde mostly converts to the hydrate $CH_2(OH)_2$. A few percent of methanol is usually added to these solutions to limit the extent of polymerization. Formaldehyde is also available as its cyclic trimer, trioxane, and as paraformaldehyde. Formalin reversibly polymerizes to produce its cyclic trimer, 1,3,5-trioxane or the linear polymer polyoxymethylene. The latter one can be heated to obtain methanol-free formaldehyde. Because of the formation of these derivatives, formaldehyde gas deviates strongly from the ideal gas law, especially at high pressure or low temperature.

Trioxane is a crystalline solid with a chloroform-like odor. It is soluble in water, alcohols, ketones, ether, acetone, chlorinated and aromatic hydrocarbons, and other organic solvents and slightly soluble in pentane, petroleum ether, and lower paraffins. In nonaqueous systems, trioxane readily converts to monomeric formaldehyde. Paraformaldehyde is available as a powdered or flaked product containing the equivalent of 91% to 93%

formaldehyde, a maximum of 9% water, and a maximum of 0.03% acidity as formic acid. It is soluble in fixed alkali hydroxide solutions, slowly soluble in cold water, more readily soluble in hot water with evolution of formaldehyde vapors, and insoluble in alcohol and ether. Formaldehyde gas can be regenerated from paraformaldehyde by heating (IARC 1982, 1995, ATSDR 1999).

3.5. Carcinogenicity

Formaldehyde (gas) is reasonably anticipated to be a human carcinogen based on limited evidence of carcinogenicity in humans and sufficientevidence of carcinogenicity in experimental animals (IARC 1982, 1987, 1995).

Excess incidences of nasopharyngeal cancers in humans were observed in two of six cohort studies, three of four case-control studies, and in meta-analyses. In addition, two of three case-control studies showed a positive association between occupational exposure to formaldehyde and squamous-cell carcinomas of the nasal cavities and paranasal sinuses. Three other case-control studies examined cancer (unspecified cell type) of the nasal cavity and paranasal sinuses; two studies presented negative results, but one showed weak positive results. The overall observed incidences of cancers of the nasal cavities and paranasal sinuses in occupational cohorts were lower than expected. The occurrence of these cancers showed an exposure-response gradient in more than one study; however, the numbers of exposed cases were often small, and there was a lack of consistency between cohort and casecontrol studies. Cohort studies of embalmers and other professionals that use formaldehyde showed some excess risk for brain cancer. The available epidemiological data did not show an excess risk for oropharyngeal, laryngeal, lung, lymphatic, or hematopoietic

cancers. The slight excesses of cancer among professionals noted in several studies generally did not display the patterns of increasing risk with various measures of exposure (i.e., latency, duration, level, or cumulative) typically seen for occupational carcinogens. No other cancer showed consistent excess incidences across the various studies (IARC 1987, 1995).

When administered by inhalation, formaldehyde induced squamous cell carcinomas of the nasal cavity in rats of both sexes. Inhalation studies in hamsters or mice did not show evidence of carcinogenicity or were inadequate for evaluation. Rats administered formaldehyde in drinking water had increased incidences of forestomach papillomas in one study and leukemia and gastrointestinal tract tumors in another (IARC 1995).

3.6. Use

The primary uses for formaldehyde are for the production of ureaformaldehyde resins (23%), phenolic resins (19%), acetylenic chemicals (12%), polyacetal resins (11%), methylene diisocyanate (6%), pentaerythritol (5%), urea-formaldehyde concentrates (4%), hexamethylenetetramine (4%), melamine resins (4%), and miscellaneous products (chelating agents, trimethylolpropane, pyridine chemicals, nitroparaffin derivatives, textile treatings, and trimethylolethane) (12%). Urea-formaldehyde resins and phenolformaldehyde resins are used primarily as adhesives in the manufacture of particle board, fiberboard, and plywood, and for molding, paper treating and coating, textile treating, surface coating, and foams for insulation. The percentage of total formaldehyde production used in urea-formaldehyde resins and phenolformaldehyde resins have ranged between 20% and 26% each since the early 1960s (IARC 1982, 1995, ATSDR 1999).

Formaldehyde is used in relatively small quantities for preservationand disinfection. These include disinfecting hospital wards, dwellings, ships, storage houses, utensils, and clothing; preserving and embalming biological specimens; sterilizing soil; as a germicide, insecticide, and fungicide; and as an antibacterial agent in soaps, shampoos, hair preparations, deodorants, lotions, make-up, mouthwashes, and nail products (IARC 1995, ATSDR 1999).

Compounds produced from formaldehyde have many applications. Polyacetal plastics are used in automobiles and in audio and video electronics equipment; pentaerythritol is used in surface coatings and explosives; hexamethylenetetramine is used as a crosslinking agent for phenol-formaldehyde resins and in explosives; and nitrilotriacetic acid and ethylenediaminetetraacetic acid are chelating agents and are used in some detergents. Other compounds are used to manufacture polyurethane and polyester plastics, synthetic resin coatings and lubricating oils, plasticizers, dyes, tanning agents, extraction agents, crop protection agents, animal feeds, perfumes, vitamins, flavorings, and drugs (IARC 1982, 1995).

3.7. Production

Industrially, formaldehyde is produced by the catalytic oxidation of methanol. The most common catalysts are silver metal or a mixture of an iron oxide with molybdenum and vanadium. In the more commonly used FORMOX® process methanol and oxygen react at ca 250-400 °C in presence of iron oxide in combination with molybdenum and/or vanadium to produce formaldehyde according to the chemical equation:

$$2\ CH_3OH + O_2 \rightarrow 2\ H_2CO + 2\ H_2O$$

The silver-based catalyst is usually operated at a higher temperature, about 650 °C. On it, two chemical reactions simultaneously produce formaldehyde: the one shown above, and the dehydrogenation reaction:

$CH_3OH \rightarrow H_2CO + H_2$

Formaldehyde is readily oxidized by atmospheric oxygen to form formic acid. Formic acid is found in ppm levels in commercial formaldehyde. On a smaller scale, formalin can be produced using a whole range of other methods including conversion from ethanol instead of the normally-fed methanol feedstock. Such methods are of less commercial importance.

3.8. Exposure

Formaldehyde is released to the environment from bothanthropogenic and natural sources. The primary routes of potential human exposure to formaldehyde are inhalation and dermal contact. Formaldehyde does occur naturally in fruits and some foods, and it is formed endogenously in mammals, including humans, as a consequence of oxidative metabolism of many xenobiotics.

Combustion processes account for most of the formaldehyde released to the environment. These include automobile exhausts, power plants, incinerators, refineries, wood stoves, kerosene heaters, and cigarettes. Indirect sources include photochemical oxidation of hydrocarbons (especially methane) and other formaldehyde precursors released from combustion sources (IARC 1982, 1995, ATSDR 1999). According to EPA's Toxic Chemicals Release Inventory (TRI), annual environmental releases of formaldehyde totaled 17.2 million to 24.9 million lb between 1988 and 1999 with the majority (50% to 66%) released to the atmosphere. Releases for 1999 were approximately 24.2

million lb from 849 facilities; however, the top two facilities accounted for 42% of the total (TRI99 2001). Formaldehyde has a short half-life in the environment because it is removed from the air by photochemical processes and precipitation and biodegradation.

Most of the formaldehyde produced in the United States is synthesized from methanol in closed automated process systems; therefore, the risk of exposure during production is minimized. Potential occupational exposure may occur during the production of end products in which formaldehyde and its solutions are used, in the garment industry, during various preservation processes, and in laboratories. Health care professionals such as pharmacists, physicians, veterinarians, dentists, and nurses may be exposed to vapors during the preparation, administration, or clean up of medicinal products. Patients who receive the medicines are directly exposed. Pathologists and histology technicians, and teachers and students who handle preserved specimens represent potential high-exposure groups (ATSDR 1999, HSDB 2001).

The National Occupational Exposure Survey (1981-1983) indicated that 1,329,332 workers were potentially exposed to formaldehyde (ATSDR 1999). The National Occupational Hazard Survey, conducted by NIOSH from 1972 to 1974, estimated that 1.6 million workers were exposed to formaldehyde in more than 60 industrial categories. Of these workers, approximately 57,000 were exposed for 4 hours or more per day. Nearly one-third (507,200) were engaged in medical and other health services, and another third (457,200) were in the following categories: chemicals and allied products, printing and publishing, paper and allied products, machinery (other than electrical), retail general merchandise, automotive dealers and service stations, eating and drinking establishments, and personal services (i.e., funeral

services and crematoriums, photographic studios, and dry cleaning plants) (NIOSH 1976, 1981).

The general population may be exposed to formaldehyde through its use in construction materials, wood products, textiles, home furnishings, paper, cosmetics, cigarette smoke, and pharmaceuticals. Formaldehyde released to indoor air from construction materials, furnishings, and cigarettes are major sources of exposure. Cigarettes may contribute as much as 10% to 25% of the indoor exposure. Automobile exhaust is a major source of formaldehyde in ambient air. In addition, formaldehyde can be absorbed through the skin from cosmetics or contact with other consumer products containing formaldehyde. Subpopulations with particularly high potential for formaldehyde exposure include the 2.2 million residents of mobile homes containing particle board and plywood, the 1.7 million persons living in conventional homes insulated with urea-formaldehyde foam, and resins (CHIP 1979, Chem. Eng. News 1984, ATSDR 1999). Individuals who come in contact with large amounts of unwashed permanent press fabrics treated with formaldehyde-releasing resins (CHIP 1979, Chem. Eng. News 1984, ATSDR 1999).

3.9. Current state of the H_2CO spectroscopic studies

In order to verify the uniqueness of the work is important to perform bibliographic research on the topic, to find what has been previously studied. There are over four hundred articles dealing with the rotational-vibrational spectra of formaldehyde but unfortunately not all of these studies are accurate enough. This fact has been one of the other reasons for this study – to rectified and complete the data about this molecule.

The previous studies on this topic are related mainly to the electronic spectroscopy. Several infrared studies of the ν_4, ν_6, ν_3 and ν_2 bands have been reported previously – mainly experimentaly obtained pure vibrational energy levels. In fact, formaldehyde is one of the most extensively studied molecules also by microwave spectroscopy (in the microwave region of electromagnetic spectra) and their rotational transitions within the ground vibrational state have already been studied as well.

4. Theoretical background

A molecule of formaldehyde belonging to the symmetry group C_{2v} has four vibrational modes, whose energy levels overlap to the microwave area of the electromagnetic spectrum and on **Figure 4-1** we can see the corresponding vibrational bands ν_4 (out-of-plan band), ν_6 (CH_2 rock), ν_3 (CH_2 band) and ν_2 (CO stretch), another possible transcription of these interacting vibrational states is 4^1, 6^1, 3^1 and 2^1. However, this relatively simple molecule has a big problem with strong resonances – there is a so-called "triangular type" of the system of interacting Coriolis forces. To put it simply, the movements of this molecule have a considerable influence on the principal moments of inertia, so the constants A, B, and C in the excited vibrational state significantly differ from those in the ground state.

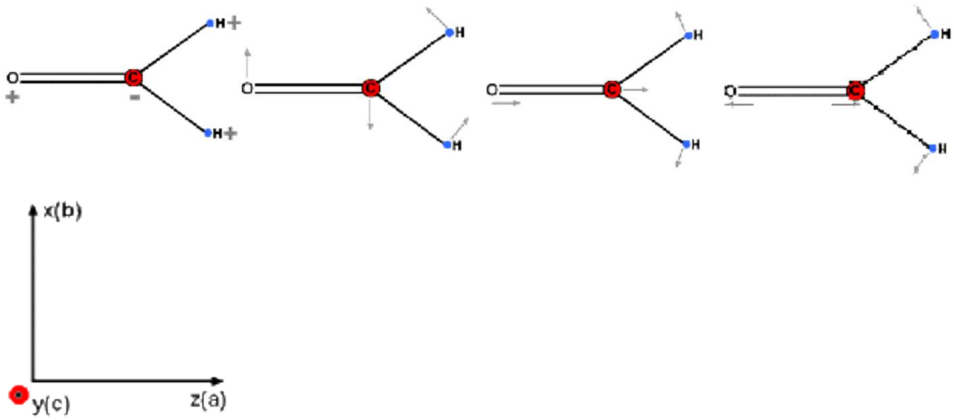

Figure 4-1: *The four vibrational modes of the formaldehyde studied in this work. From the left: ν_4 (out-of-plan band), ν_6 (CH_2 rock), ν_3 (CH_2 band) and ν_2 (CO stretch).*

All these levels are very strongly resonating, whether it is an A-type Coriolis resonance between the excited vibrational states 4^1 and 6^1, B-type Coriolis resonance between the excited vibrational states 3^1 and 4^1 or a seemingly negligible C-type

Coriolis resonance between the excited vibrational states 3^1 and 6^1. In addition, there is a type of anharmonic interaction between the excited vibrational states 3^1 and 2^1. The absorption maxima of vibration levels obtained from previous infrared studies reach the frequencies for ν_4 (1167.256 cm^{-1}), ν_6 (1249.094 cm^{-1}), ν_3 (1500.174 cm^{-1}) and for ν_2 (1746.009 cm^{-1}), as shown schematically in **Figure 4-2**.

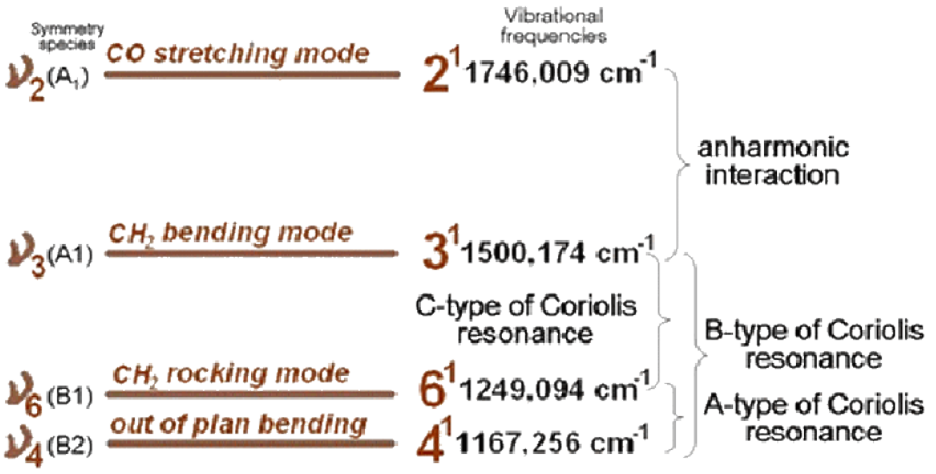

Figure 4-2: *Vibrational energy levels of formaldehyde – vibrational modes and their corresponding frequencies. The movement of this molecule has a strong effect on the principal moments of inertia and hence A, B, C constants differ significantly in the excited vibrational states from those in the ground vibrational state.*

4.1. Rigid rotor

Because the rate of change of the rotational state is usually much lower than the change of the vibrational or the electronic state, in the first approximation the studied molecule can be seen as a rigid body – a rotor, whose individual material points – the atomic nuclei – are located in the middle positions designated by averaging over the far faster vibrational and electronic movements. As a result, there is an option to separate the

individual members of the total molecular Hamiltonian and to deal only with the rotational Hamiltonian in the first approximation. To eliminate the contribution of the kinetic energy associated with translation of the molecule due to the *laboratory-fixed system* of the axes, it is possible to choose the new Cartesian coordinate system – *molecule-fixed system* that will move the center of gravity of the molecule, will not rotate together with the molecule and whose origin will be located in the center of gravity of the molecule. From the perspective of classical mechanics, rotational energy of the rigid rotor can be expressed by the relation:

eq. 4-1:

$$T = \frac{1}{2}\sum_{\alpha,\beta} I_{\alpha\beta}\omega_\alpha\omega_\beta$$

where ω is the angular speed of the non-rotating molecule-fixed system moving with the centre of gravity of the molecule relative to the molecule-fixed system rotating with a rigid nuclear skeleton of the molecule (α, β = *x, y, z*) and where the components of the inertia tensor *I* are defined by the expressions:

eq. 4-2:

$$I_{xx} = \sum_i m_i(y_i^2 + y_i^2)$$

eq. 4-3:

$$I_{xy} = -\sum_i m_i x_i y_i$$

The expression for kinetic energy can be further simplified by transforming the inertia tensor into the main axes, where deviation moments $I_{\alpha\beta}$ equal zero. Components of the moment of

inertia in the main axes I_α can also be found by solving the determinant equation:

eq. 4-4:

$$\begin{vmatrix} I_{xx} - I_\alpha & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} - I_\alpha & I_{yz} \\ I_{xy} & I_{yz} & I_{zz} - I_\alpha \end{vmatrix} = 0$$

Classical mechanics also introduces the angular momentum that we define as:

eq. 4-5:

$$J_\alpha = \frac{\partial T}{\partial \omega_\alpha} = I_\alpha \omega_\alpha;$$

and that can be easily applied to the formulation of the quantum mechanical expression for rotational Hamiltonian H, which allows to formulate the rotational Schrödinger equation providing the energy of a general rigid rotor E_r:

eq. 4-6:

$$H\psi = \left\{(\hbar^2/2I_x)J_x^2 + \left(\hbar^2/2I_y\right)J_y^2 + (\hbar^2/2I_z)J_z^2\right\}\psi = E_r\psi$$

where the original angular momenta J_α measuring $\hbar$ are now represented as dimensionless. The equation (eq. 4-6) is conventionally rewritten by renaming the axes *x, y, z* to *a, b, c,* so that for the main moments of inertia applies:

eq. 4-7:

$$I_a \leq I_b \leq I_c$$

The Hamiltonian in the equation (eq. 4-6) can be then rewritten as:

eq. 4-8:

$$H\psi = \hbar^{-2}\{AJ_a^2 + BJ_b^2 + CJ_c^2\}$$

where $\hbar = h/2\pi$ is the so-called reduced Planck constant and *A, B, C* are the rotational constants:

eq. 4-9:

$$A = \hbar^2/2I_a$$
$$B = \hbar^2/2I_b$$
$$C = \hbar^2/2I_c$$

for which, of course, applies:

eq. 4-10:

$$A \geq B \geq C$$

The rotational constants introduced by equations (eq. 4-1) to (eq. 4-9) are in units of energy [J] (of course, when the corresponding constants and units are used). The equations (eq. 4-1) to (eq. 4-9) divided by Planck's constant have the dimension of frequency [Hz], which is typical for use in microwave spectroscopy.

4.2. Rotational spectra

Every experimentally rotational spectrum obtained provides a set of transition frequencies that are interpreted in term for relevant energy levels and appropriate selection rules. The rotational spectra theory is based on the total molecular Hamiltonian and corresponding Schrödinger equation. The total molecular Hamiltonian is defined in the Cartesian coordinates system *(X, Y, Z)* with the origin and axis orientation fixed in space and contains terms describing explicitly the kinetic and electrostatic potential energy of electrons and nuclei and all the effects arising from the electron and nuclear spin existence. The individual contributions to the total energy of the molecule can be expressed through the angular momentum operators. In the general case, angular momentum appearing in the total molecular Hamiltonian are follows:

- rotational angular momentum of the bare nuclei ***R***
- total electronic orbital angular momentum $\boldsymbol{L} = \sum_j l_j$, where l_j is orbital angular momentum of *j*-th electron
- vibrational angular momentum ***p***
- total electron spin angular momentum $\boldsymbol{S} = \sum_j s_j$, where s_j is spin angular momentum of *j*-th electron
- total nuclear spin angular momentum $\boldsymbol{I} = \sum_i I_i$, where I_i is nuclear spin angular momentum of *i*-th nucleus

Spin angular momentum magnitude is defined by spin quantum number, shortly spin, $s = \frac{1}{2}$ for electrons and *I* for nuclei, which takes integer or half-integer values. Particles called fermions possess half-integral spin while bosons have integral spin. Total electron spin quantum number S is an important characteristic for each of electronic states of molecules. The coupling of the electron spin with the electron orbital angular

momentum lead to the splitting of electronic state into $2S+1$ components and this value, called multiplicity, is written as a superscript in front of the symmetry type symbol. The multiplicity is always bigger than one for open-shell molecules.

Although the total Hamiltonian can be simplified by making a series of approximations and coordinate transformations, it refers to many electronic and vibrational state of one electronic state. For these proposes, a so called effective Hamiltonian $\widehat{H}_{eff}$ acting only in these states is constructed. The effective Hamiltonian operates on a suitable set of basic functions specified by quantum numbers that arise directly from the spectrum. Subsequently, its eigenvalues (energy values) are searched by the process of diagonalization of the $\widehat{H}_{eff}$ matrix. Finally, the energy defferences are compared with the transition frequencies observed.

The effective Hamiltonian $\widehat{H}_{eff}$ always includes terms representing various interactions within the molecule which are relevant for given molecule and type of experiment. Each term is composed form the molecular paramerers multiplied ba the angular momentum operators and has to satisfy physical and symmetry requirements. Effective Hamiltonian is derived from the total molecular Hamiltonian usually by the perturbation theory. The perturbation calculations are made to eliminate the matrix elements connection different electronic and vibrational states. Their effects are then absorbed to the molecular constants appearing in $\widehat{H}_{eff}$.

The resultant effective Hamiltonian is usually defined in the molecule-fixed co-ordinate system (*x, y, z*) with origin in the molecular center of mass. The set of the space-fixed axes (*x, y, z*) is rotating with molecule and is turned in respect to the space-fixed

axes (*X, Y, Z*) by the three Euler angles θ, ϕ, χ. The transformation between both of the axis system is for *i*-th particle as follows:

eq. 4-11:

$$R_i = R_0 + P^{-1}(\theta, \phi, \chi) r_i$$

Where R_i is the position vector of the i-th particle with respect to (X, Y, Z), R_0 is a vector containing the space-fixed coordinates of the molecular center of mass, P is a 3 × 3 matrix of direction cosines relating the orientation of the molecule-fixed axes to the space-fixed ones and r_i position vector of the i-th particle with respect to (x, y, z).

5. Experimental background

The following section provides a brief preview of the experimental technique in rotational spectroscopy and a specific experimental arrangement for detection in the millimeter and submillimeter areas. Similar experimental systems can be found only in a few laboratories in Europe. In addition to its specific properties, microwave spectroscopy has a number of experimental differences from other types of molecular spectroscopy, for example, the use of tunable sources of monochromatic radiation.

When it comes to the basic elements of the spectrometer operating in the infrared, visible or ultraviolet areas, a person knowledgeable of the physico-chemical analytical methods will mostly think of the diffraction grating, dispersive prism, entrance and exit slits and the mirror. However, this does not apply to the microwave spectrometer, which does not use any of these elements, since it mainly uses a tunable source of monochromatic radiation (except for the Fourier transform microwave spectrometers). A microwave spectrometer in its simplest form consists of three basic components: ***a microwave source***, ***an absorption cell*** containing the examined sample and a ***detector***. Modification of the radiation passed through the sample is amplified electronically and stored in the computer memory as a function of the radiation frequency providing the microwave spectrum.

To examine the ground vibrational state of the molecule H_2CO in the gas phase, an experimental technique of highly differentiated millimeter and submillimeter spectroscopy was used, specifically the Lille MMW spectrometer of the PhLAM laboratory at the Lille 1 University shown schematically on the **Figure 5-1**.

The estimated frequency deviation of the Lille MMW spectrometer is less than 30 kHz.

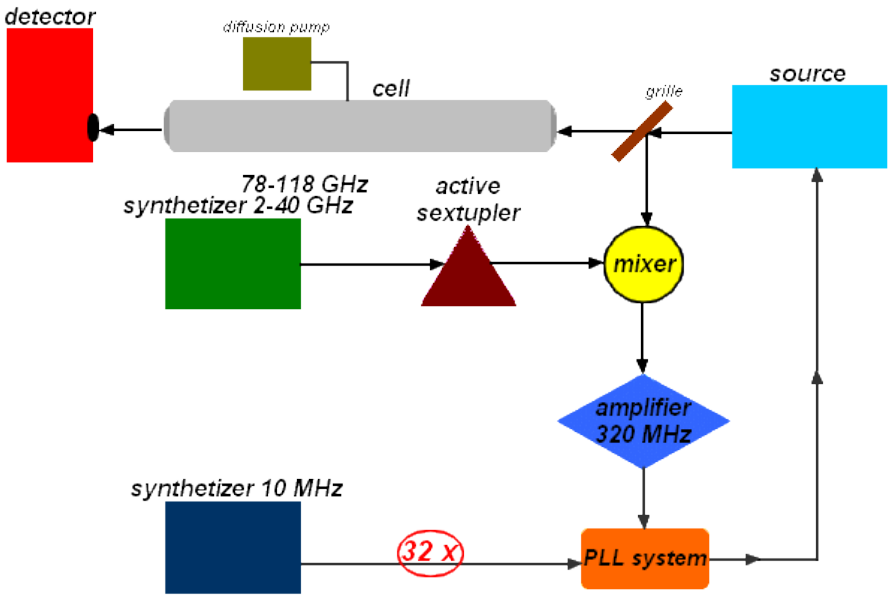

Figure 5-1: *One of the used experimental arangement of the Lille millimeter-wave spectrometer.*

5.1. Source of MW radiation

As a tunable source of coherent microwave radiation, two BWO* tubes from the Russian company ISTOCK were used, which work in the area of 150-250 GHz and 520-660 GHz of the electromagnetic spectrum, and one BWO tube from the French company THOMSON, working in the area of 420-470 GHz of the electromagnetic spectrum.

* *BWO = backward wave oscillator (karcinotron)*

5.2. Detector

The most commonly used microwave radiation detector is thermally conductive detector called ***bolometer***, whose basic component is a short metal wire (barretter) or a semiconductor

bead (thermistor) cooled by liquid helium, which is heated only by exposure to microwave radiation, thus changing its resistance [11]. One of the biggest advantages of the bolometer is the linear response to the incident energy, its wide working range (over hundreds of GHz) and low electronic noise at low modulation frequencies. The disadvantages are its high operating and acquisition costs. To detect the radiation in the described experiment, a liquid helium cooled InSb bolometer was used.

5.3. Absorption cell and sample

Several kinds of measuring cells are used in microwave spectroscopy, the choice of which depends on the type of the specific experiment. In the case of this experiment, a special polytetrafluoroethylene (Teflon) absorption cell was used with the length of 150 cm and a diameter of 15 cm.

As the sample, the powder of paraformaldehyde (CH_2O) was used, which has been heated to a temperature of 200 °C in order for us to obtain from the reaction a product of formaldehyde in the gas phase, so the substance was freshly prepared before each measurement. Partial pressure of the sample in the cell was measured using a pressure sensor and the optimal pressure value was set to the range 0.015-0.024 Torr.

6. Results and discussion

The main problem, which partly impeded the achievement of results in the experimental part of the study, was specifically the problem of very low intensities of the lines in the first excited vibrational states. **Figure 6-1** shows the specific lines that were measured with the Lille spectrometer in the area of 150 to 660 GHz and that make obvious the problem with the line intensity. The lines with the highest intensity lie in the frequency region around 400 GHz to 650 GHz, but there are only few of them (designated by arrows in the image); most of the lines, on the other hand, have a very low intensity. Such data of lines with the intensity problem is very difficult to process: two lines of this type that are almost merging with the noise can be seen on **Figure 6-2**. Therefore, it is appropriate to perform a few repetitions and to take into account the inaccuracy of measurement when verifying the data in the program [12]. The intensity problem often arises also in marginal areas of measuring tubes, where it is further boosted by the overall instability of the measuring equipment.

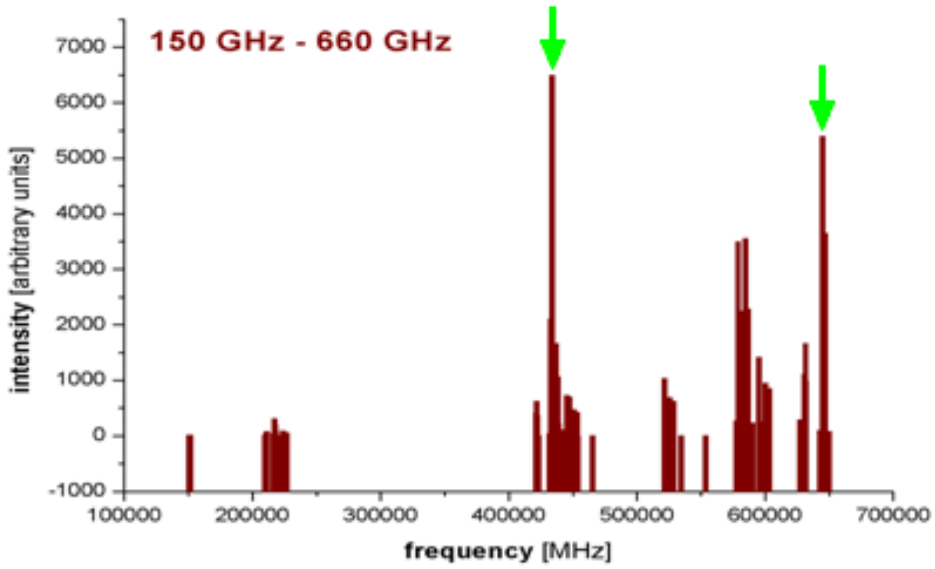

Figure 6-1: *The real lines of formaldehyde measured in Lille, the most intense lines are shown by green arrows.*

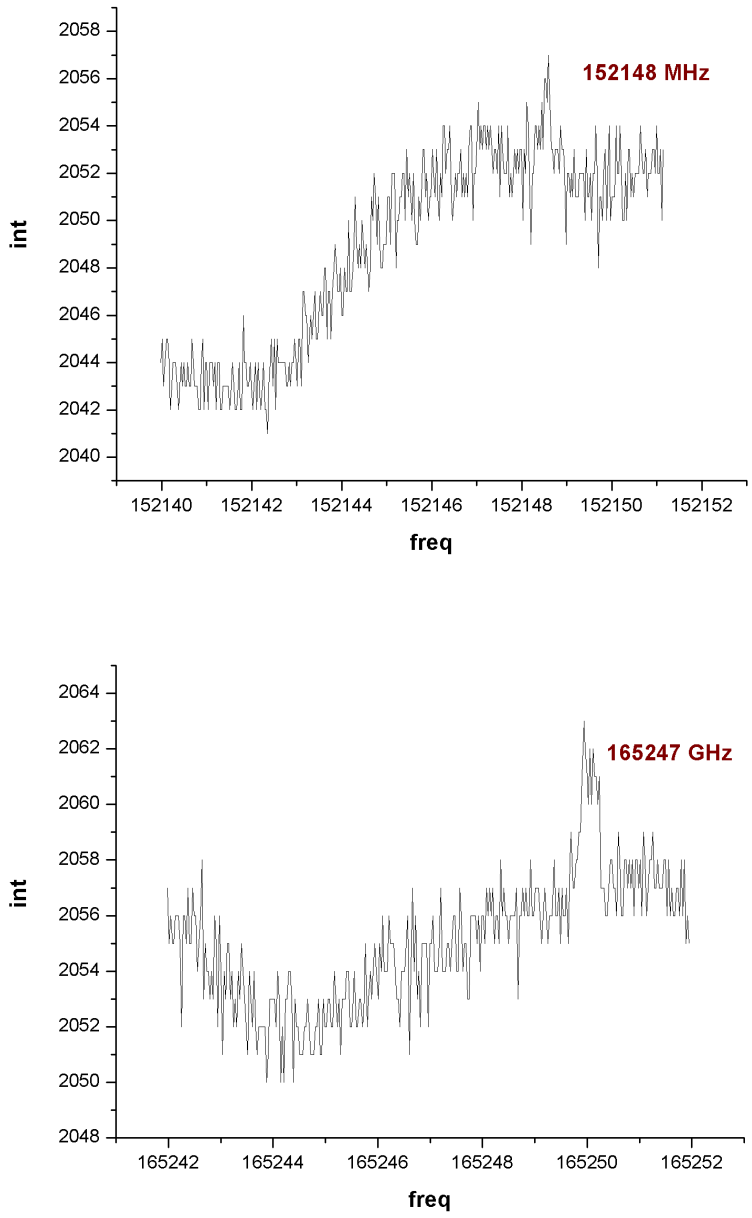

Figure 6-2: *The concrete recorded lines of formaldehyde in the first vibrational excited state – very low intensity and unstable background of the spectrometer.*

Another interesting feature is the possible presence of various isotopic forms of carbon, which can, however, cause more difficulties in processing the spectra. If we tune the specific area where we expect the line to be in accordance with our precalculated values and two lines appear on the site that have

similar frequency distance and similar high intensity, it means we have a problem with the determination, which of these two lines actually matches the sought transition and whether it corresponds to our substance at all (Fig. 10-2). One of the possible reasons may be the presence of a line of another isotope, which happened in our study, where it was the presence of formaldehyde with an isotope of carbon ^{13}C, i.e., the molecule $H_2{}^{13}C^{16}O$ (the line in the image marked with an arrow). Since ^{13}C is a stable isotope of carbon and its natural amount is around 1.1% of the total amount of natural carbon (all isotopes) on Earth, it is quite likely that we can come upon this isotope also in the spectrum (note: of the 100 measured lines, roughly one line may belong to the isotope ^{13}C). This fact can be verified by using the free database of the JPL Molecular Spectroscopy catalogue of the NASA Jet Propulsion Laboratory, California Institute of Technology.

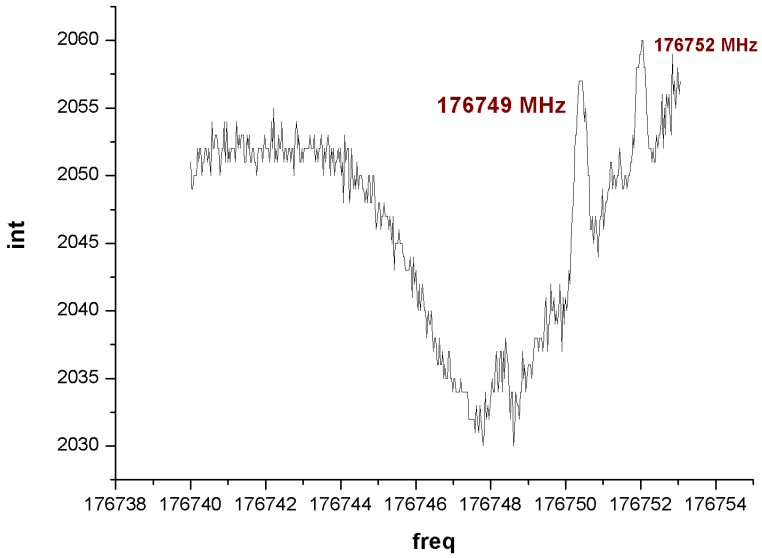

Figure 6-3: *The concrete recorded lines of formaldehyde – two different isotopic species. The frequency of 176,749 GHz corresponds to the main isotopic specie with carbon-12; the frequency of 176,752 GHz corresponds to the less abundant stable isotope with carbon-13.*

The results of these measurements has been than combined with the 2^1, 3^1, 4^1 and 6^1 infrared energy levels, which has been obtained from previous analysis of FTS spectra of the ν_4, ν_6 and ν_3 bands recorded in 10 μm region and more recently for the ν_2 fundamental band. The energy level calculation of the 2^1, 3^1, 4^1 and 6^1 interacting states accounts for the various Coriolis-type resonances that perturb the energy levels of the 2^1, 3^1, 4^1 and 6^1 vibrational states as well as for the anharmonic resonances coupling the 2^1 and 3^1 energy levels, and in this way the microwave and infrared data could be reproduced within their associated experimental uncertainty. However, it is clear that the theoretical model used to account for the very large A-type Coriolis resonance linking the 4^1 and 6^1 energy levels of H_2CO is only effective with poor physical meaning.

7. Related publications

[1] L. Margules, A. Perrin, R. Janeckova, S. Bailleux, C. P. Endres, T. F. Giesen and S. Schlemmer, *Canadian Journal of Physics* **2009**, *87*, 425-435.

Rotational transitions within the 2^1, 3^1, 4^1, and 6^1 states of formaldehyde $H_2{}^{12}C^{16}O$ [1]

L. Margulès, A. Perrin, R. Janečkovà, S. Bailleux, C.P. Endres, T.F. Giesen, and S. Schlemmer

Abstract: This work, besides its fundamental interest, is motivated by the atmospheric and astrophysical importance of formaldehyde (H_2CO). The goal of this study is to complete the already existing list of rotational transitions within the ground vibration state by a list of transitions within the four first excited 2^1, 3^1, 4^1, and 6^1 vibrational states, to help the detection of this species by microwave or millimetre wave techniques. For this purpose, the rotational spectra of H_2CO in the 2^1, 3^1, 4^1, and 6^1 excited vibrational states have been investigated in Lille and Cologne in the millimetre region at 160–600 GHz and 850–903 GHz, respectively. The results of these millimetre wave measurements were combined with the 2^1, 3^1, 4^1, and 6^1 infrared energy levels, which were obtained from previous analysis of FTS spectra of the ν_4 (out of plane bending mode), ν_6 (CH_2 rock mode), and ν_3 (CH_2 bending mode) bands recorded in the 10 μm region (D.C. Reuter, S. Nadler, S.J. Daunt, and J.W.C. Johns. J. Chem. Phys. **91**, 646 (1989)) and more recently for the ν_2 fundamental band (C=O stretching, located at 1746.009 cm^{-1}) (F. Kwabia Tchana, A. Perrin, and N. Lacome. J. Mol. Spectrosc. **245**, 141, (2007)). The energy level calculation of the 2^1, 3^1, 4^1, and 6^1 interacting states accounts for the various Coriolis-type resonances that perturb the energy levels of the 2^1, 3^1, 4^1, and 6^1 vibrational states as well as for the anharmonic resonances coupling the 2^1 and 3^1 energy levels, and in this way the microwave and infrared data could be reproduced within their associated experimental uncertainty. However, it is clear that the theoretical model used to account for the very large A-type Coriolis resonance linking the 4^1 and 6^1 energy levels of H_2CO is only effective with poor physical meaning.

PACS No: 33.20.Sn

Résumé : En dehors de son intérêt théorique, ce travail, est motivé par le rôle important joué par le formaldéhyde (H_2CO) dans la chimie de la troposphère terrestre et parce que cette molécule a été détectée dans de nombreux objets astrophysiques. Le but de ce travail est de compléter la liste, déjà existante, de transitions rotationnelles du formaldéhyde dans l'état vibrationnel fondamental par une liste complémentaire de transitions rotationnelles dans les quatre premiers états vibrationnels excités 2^1, 3^1, 4^1 et 6^1 de H_2CO. Le but est de permettre la détection de cette espèce dans des états vibrationnels excités par technique micro-onde ou submillimétrique. Pour cela le spectre rotationnel de H_2CO dans les états excités 2^1, 3^1, 4^1, et 6^1 a été mesuré à Lille et Cologne dans le domaine millimétrique (à 160–600 GHz et 850–903 GHz, respectivement). Les résultats de ces mesures ont été combinés avec les niveaux d'énergie infrarouges pour les états 2^1, 3^1, 4^1, et 6^1 obtenus précédemment lors d'analyses de spectres enregistrés par transformée de Fourier à haute résolution pour les bandes ν_4 (ouverture angulaire hors plan du groupe CH_2), ν_6 (torsion dans le plan de CH_2) et ν_3 (ouverture angulaire symétrique de CH_2) enregistrés à 10 μm (D.C. Reuter, S. Nadler, S.J. Daunt, and J.W.C. Johns. J. Chem. Phys. **91**, 646 (1989)) et plus récemment pour la bande ν_2 (élongation C = O), située à 1746 009 cm^{-1}) (F. Kwabia Tchana, A. Perrin, and N. Lacome. J. Mol. Spectrosc. **245**, 141, (2007)). Le calcul de niveaux d'énergie pour les états vibrationnels inter agissants 2^1, 3^1, 4^1 et 6^1 tient compte des différentes résonances de type Coriolis qui perturbent les niveaux d'énergie des états 3^1, 4^1 et 6^1 ainsi que des résonances anharmoniques qui couplent les niveaux des états vibrationnels 2^1 et 3^1. De cette façon, l'ensemble des mesures micro-ondes et niveaux d'énergies infrarouges ont pu être reproduits à leurs précisions expérimentales respectives. Cependant, il est clair que le modèle théorique utilisé pour tenir compte de la forte résonance de Coriolis de type A qui couple les niveaux d'énergie des états 4^1 et 6^1 de H_2CO est purement effectif et donc de peu de signification réellement physique.

1. Introduction

Formaldehyde, both its main isotopic species $H_2{}^{12}C^{16}O$ and its deuterated variants $HD^{12}C^{16}O$ and D_2CO, was detected by microwave techniques in numerous astrophysical objects. For example, this species was observed in the Orion molecular cloud and in various low-luminosity protostars ([1, 2] and refs. cited therein).

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CHAPTER II

PHOTOACOUSTIC SPECTROSCOPY OF THE $C_7H_{14}O_2$

CO_2–laser photoacoustic absorption spectroscopy of the molecule of n–penthylacetate in the gas phase investigated by photoacoustic detection (PAS) for concentration analyses.

8. Introduction to Chapter II

The CO_2-laser photoacoustic detection technique is a suitable spectroscopic method for analysis of the concentration of substances in gas phase applicable both in laboratory conditions and for direct detection in the ambient atmosphere. It is therefore very useful, for example, for detection of harmful substances, monitoring of their spread in the atmosphere, which is often used in safety engineering.

In this part of the study, the absorption spectra of n-pentyl acetate in the gas phase were explored using Fourier transform infrared spectroscopy (FTIR) and CO_2-laser photoacoustic spectroscopy (PAS) for subsequent simulation of the spread of matter representing the nerve gas (sarin) inside of the boundary layer of the modelled atmosphere. For the photoacoustic detection of n-pentyl acetate in the gas phase, three emission lines of CO_2-laser with a detection limit 1-3 ppm were used.

9. Motivation and previous studies

The species studied in this chapter is a molecule of n-pentylacetate and it is appropriate to mention why the study with this molecule was conducted. The very substance of the gaseous n-pentylacetate (n-amyl acetate; $C_7H_{14}O_2$) was already in the past and also recently used in dispersion studies [13] instead of the nerve gas sarin ($C_4H_{10}FO_2P$), which was one of the motivational factors of this study. The extremely toxic substance, which is used as a nerve gas, is represented here by its non-toxic substitute with similar physico-chemical properties, such as vapor pressure, boiling point and molecular weight. Another motivation for this study was the possible use of photoacoustic spectroscopic technique for the analysis of the trace amount of gas and subsequent use for modeling experiments simulating the spread of gaseous substances inside the wind tunnel [14]. As the tools for various simulations, such models of nerve gases are very important for risk assessment and research in safety engineering.

In fact, there are only a few spectroscopic studies on n-pentyl acetate in gas phase in the infrared region of the spectrum [15-17], however, these are primarily experimental studies carried out using the Fourier transform infrared spectroscopy technique; some further information can be obtained from the NIST database [18]. There was another diffusion study that used physical modeling for simulating the spread of toxic substance (its substitute) and included visualization of its diffusion in urban area, namely, the Old Town Square in Prague in a scale of 1:160 (urban scale) [13], where the choice of the substituent and the similarity of the two molecules are also described quite thoroughly. Based on all available information it can be said that the CO_2-laser photoacoustic spectrum of n-pentyl acetate in gas phase was recorded for the first time.

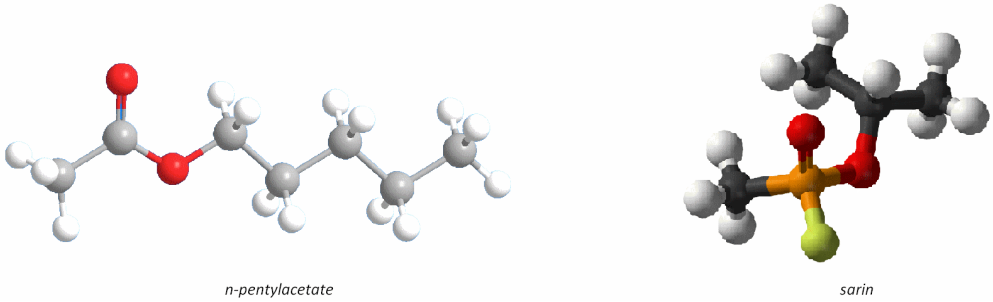

Figure 9-1: *An approximate geometry of the molecule of n-penthylacetate and molecule of sarin.*

10. Experimental background

Laser photoacoustic spectroscopy (PAS) is a technique that uses a laser as the source of radiation (e.g. a CO_2 laser like in this study) – either in the continuous or pulsed mode [19]. The principle of the PAS technique is based on recording of the pressure changes induced in a closed space of the cell by the cyclic absorption of the radiation by molecules of gas [20]. This method can be applied to a wide range of gases (e.g. NH_3, NO, NO_2, CH_3OH, CH_3CH_2OH, $CH_3CH{=}CH_2$, C_6H_6, $CH_2{=}CH_2$) [19] that are also important in terms of combustion processes and safety engineering.

One of the most used radiation sources for applying the PAS technique is a CO_2 laser emitting in the range of 1100 to 900 cm^{-1} in the infrared spectrum roughly on 60 discrete lines each of which can be detected [21]. In this spectral range, a so-called atmospheric window is situated, which means that the total absorption coefficient of the atmosphere is minimal in this area and allows the passage of radiation with these wavelengths (including CO_2 laser radiation) without loss [19]. CO_2 laser provides sufficient power allowing to detect traces of gaseous components in a mixture.

The CO_2-laser photoacoustic detection technique is based on the principle of opto-acoustics phenomenon (OA), where in the first stage the absorption of electromagnetic radiation occurs and in the second stage, acoustic waves are generated in the cell; an important condition for the OA is a possibility for the given molecule to absorb the quantum of light radiation. The photon absorption occurs when electromagnetic radiation passes through the absorbing environment. The absorbing molecule can lose the obtained energy in three ways: emission process, vibrational

energy transfer in a collision with another molecule, collision with a molecule in which the energy of absorbed radiation is converted into kinetic energy of the both involved particles. The most frequent mechanisms in case of the PAS technique is the last mentioned, i.e. vibrational-translational (V-T) relaxation. V-T relaxation results in local increase in the temperature of the gas at the point of the passage of the electromagnetic radiation through the absorbing environment and in subsequent thermal expansion increasing the pressure [19-21].

The experimental arrangement for the CO_2-laser photoacoustic spectroscopic technique consists of fairly sophisticated equipment, which includes the following main parts: gas analyzer, which generally consists of a source of radiation, photoacoustic cell and a detector of radiation (pyrodetector), and a CO_2 laser, which is capable of emitting radiation on around 60 discrete lines in the infrared region of 9-11 μm (1100-900 cm^{-1}) and provides sufficient power to detect even trace amounts in a gaseous mixture.

In this chapter, the absorption spectra of n-pentyl acetate were examined using the method of Fourier transform infrared spectroscopy (FT IR) just as reliably as with the CO_2-laser photoacoustic spectroscopic technique (PAS). FT IR spectra of the gas recorded using the commercially available Bruker IFS 120 spectrometer in the area of 600-200 cm^{-1} confirmed the absorption maximum about 1240 cm^{-1}, which corresponds to the C-O stretch region (see **Figure 11-1**). Although the spectral area available for detection using the PAS method (1100-900 cm^{-1}) is characterized by a broader and much weaker absorption band of n-pentyl acetate (see Figure 10), the three stable emission lines of the CO_2 laser 9P(20), 9P(22) and 9P(24) were characterized as appropriate for achieving the detection limit (see Table 1) under 10 ppm, which corresponds to the level of the concentration

presupposed for using the PAS technique to set up the experiment of modelling the dispersion of gaseous substances in the wind tunnel.

Effective deployment of CO_2-laser photoacoustic detection technique requires several steps to be taken while preparing for the practical application of the method (such as tools for microanalysis of gaseous substances):

- ✓ Investigation of the absorption spectrum of the studied molecule in the area of 9-11 μm, for example, using the method of Fourier transform infrared absorption spectroscopy (FT IR), see **Figure 11-1**.
- ✓ Selection of the emission line of the CO_2 laser suitable for detection of the studied molecule and calibration of the experimental system for concentration measurements on the appropriate emission line, see **Figure 11-3**.

The advantages of the laser photoacoustic detection are its high sensitivity, selectivity, linearity of concentrations in the range of several orders, its high spectral resolution and also relatively easy transportability of the whole equipment for the potential use outside the laboratory conditions [19] (for example, for modeling of a diffusion experiment in a wind tunnel, etc.).

The production of the reference quantity of n-pentyl acetate (10-500 ppm) was ensured by the specified concentration standards [22] based on the principle of the permeation (the permeability of the material), which in this particular case were made of polyethylene and polytetrafluoroethylene (Teflon) tubes providing the concentration of the studied molecule in the gas phase from 10 to 500 ppm. Partial concentrations of a substance can be calculated from the weight loss of the permeation sample and the weight of the carrier gas according to a standard formula.

It is preferable to carry out direct monitoring in the atmosphere using the PAS technique than, for example, the FT IR method due to its higher sensitivity.

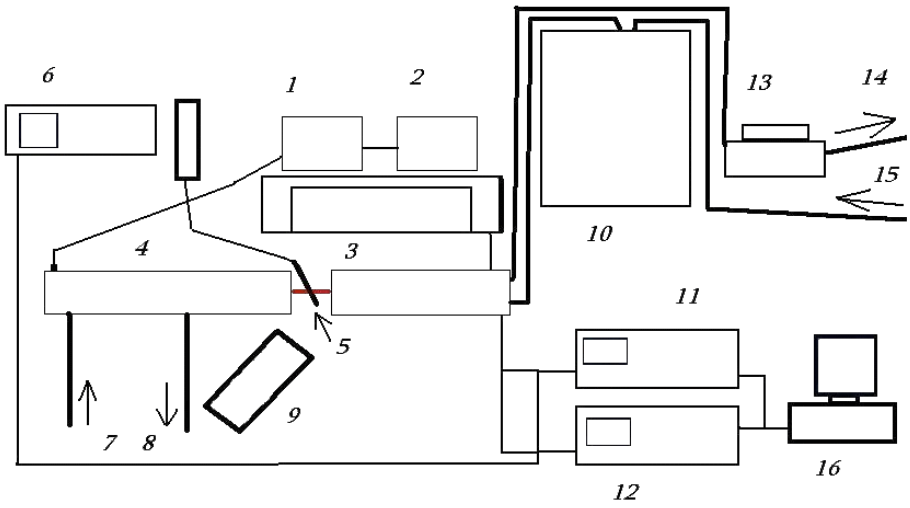

Figure 10-1: *Block diagram of experimental setting:* ***1)*** *frequency regulator of laser;* ***2)*** *power supply;* ***3)*** *photoacoustic cell;* ***4)*** *CO_2-laser (Edinburgh Instruments, type WL 8–GT);* ***5)*** *chopper;* ***6)*** *oscilloscope;* ***7),8)*** *laser cooling;* ***9)*** *CO_2 analyzer of spectra;* ***10)*** *thermostat with sample;* ***11)*** *Lock-in amplifier(a);* ***12)*** *Lock-in amplifier(b);* ***13)*** *carrier gas pumping;* ***14)*** *exhaust;* ***15)*** *suction;* ***16)*** *computer.*

11. Results and discussion

The CO_2-laser photoacoustic absorption spectrum of gaseous n-pentylacetate ($C_7H_{14}O_2$) has been investigated and recorded for the first time, on the basis of all available information. In this work, detection limit and limit of determinableness has been determined from calibration curves acquired on three relatively strong emission lines of CO_2-laser. The PAS (photoacoustic spectroscopy) experiment has been prepared for subsequent utilization as the on-line quantitative spectroscopic detection within the framework of physical simulations of the dispersion inside the modeled atmospheric boundary layer [14]. The n-pentylacetate has been used as a non-toxic substituent with similar physical-chemical characteristic of sarin ($C_4H_{10}FO_2P$).

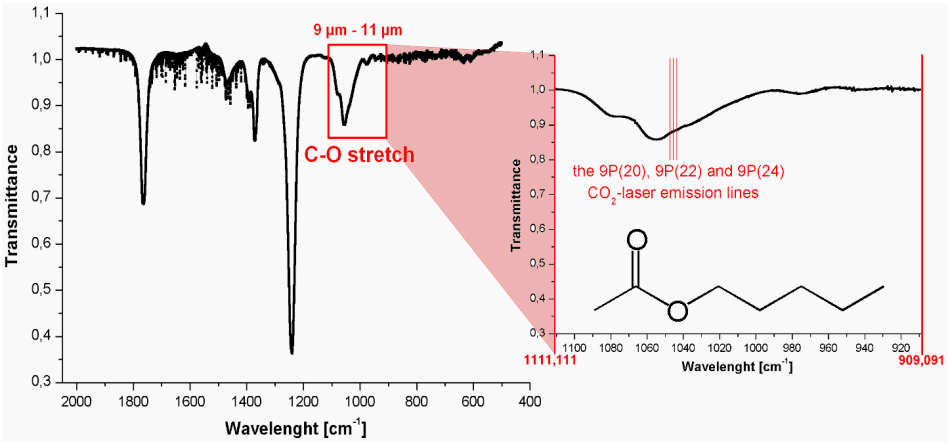

Figure 11-1: *High resolution absorption spectrum of n-pentylacetate – screening specifically through the spectral region 9-11 µm (available for PAS detection) by the FT IR method, enlarged section see on the right.*

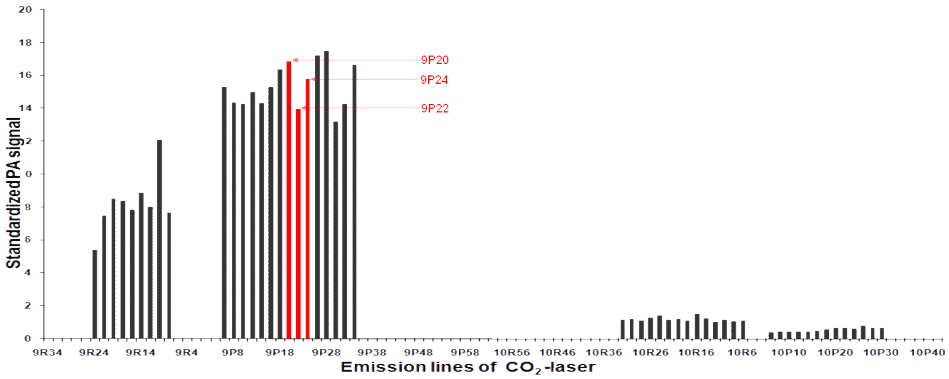

Figure 11-2: *The absorption spectrum of gaseous n-pentylacetate appointed with the aid of photoacoustic method (PAS) on the emission lines of CO_2-laser.*

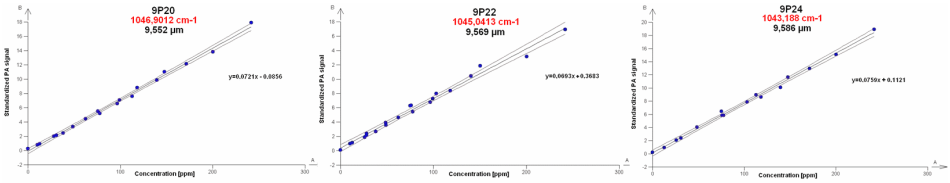

Figure 11-3: *Calibration curves for calculations of detection limit and the quantification limit (Tab. 1) - dependence of standardized photoacoustic signal on concentration; acquired amount about 10 – 300 ppm.*

CO_2-laser emission lines	detection limit [ppm]	limit of determinableness [ppm]
9P(20)	1,37	4,55
9P(22)	2,05	6,82
9P(24)	2,56	8,53

Table 11-1: *Table of detection limits and limits of determinableness on the selected CO_2-laser emission lines.*

12. Related publications

[2] L. Herecova, T. Hejzlar, J. Pavlovsky, D. Micek, Z. Zelinger, P. Kubat, R. Janeckova, V. Nevrly, P. Bitala, M. Strizik, K. Klouda and S. Civis, *Journal of Molecular Spectroscopy* **2009**, *256*, 109-110.

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CO_2-laser photoacoustic detection of gaseous *n*-pentylacetate

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ABSTRACT

The absorption spectra of gaseous *n*-pentylacetate were investigated by FT IR spectroscopy as well as CO_2-laser photoacoustic spectroscopy for simulation of the dispersion of a nerve agent (sarin) within a modeled atmospheric boundary layer. Three CO_2-laser emission lines were used for photoacoustic detection of *n*-pentylacetate with detection limit in the range of 1–3 ppm.

N-pentylacetate (*n*-amylacetate) has been recently employed in dispersion studies instead of sarin [1]. An extremely toxic nerve agent is represented by a non-toxic tracer with similar physical–chemical characteristics such as vapor pressure, boiling point and/or molecular mass. The models for nerve agents, as tools of simulation, are very important for risk estimation and for safety and security research.

There exist only a few spectroscopic studies of gaseous *n*-pentylacetate in the IR region [2–4] and information from NIST [5]. In this note, the absorption spectra of *n*-pentylacetate were investigated by FT IR spectroscopy as well as CO_2-laser photoacoustic spectroscopy (PAS). An FT IR spectrum of *n*-pentylacetate recorded by the Bruker IFS 120 spectrometer within a range of 600–2000 cm^{-1} confirmed the absorption maximum around 1240 cm^{-1} corresponding to the C–O stretch (Fig. 1a). The spectral region available for PAS detection (1100–900 cm^{-1}) is characterized by a broad and weak absorption band of *n*-pentylacetate (Fig. 1b).

Direct monitoring of *n*-pentylacetate in the atmosphere as a model of a nerve agent by the FT IR spectrometer has disadvantages due to its lower sensitivity [6]. The advantages of PAS lie, above all, in its high sensitivity, selectivity, linearity in the interval of several orders as regards concentrations, high spectral resolution and also the mobility of the setup for possible uses not only in laboratory conditions (for wind tunnel modeling dispersion experiments e.g.) [7,8].

The PAS experimental setup is a sophisticated device containing the following main parts: a gas analyzing system, which generally consists of the photoacoustic cell and radiation detector (pyrodetector), and the source of radiation—a CO_2-laser, which is one of the most widely used lasers for the photoacoustic gas detection method; this emits radiation on about 60 discrete lines in the IR region 1100–900 cm^{-1} and gives sufficient power to provide detection of gaseous components up to the trace amount. The details are described in our previous works [9–11].

A generation of trace amounts of *n*-pentylacetate was obtained by the use of precise concentration standards based on the permeation method [12]. The standards were made of polyethylene and polytetrafluorethylene (Teflon) tubes ensuring 10–500 ppm of investigated gas phase molecule. The partial concentration can be calculated from the mass decrease of the permeation sample and the flow rate of the carrier gas according to the standard equation.

The limit of detection is derived from the smallest measure x_L (expressed in concentration units) that can be detected with reasonable certainty for a given analytical procedure

$$x_L = k\sigma, \tag{1}$$

where σ denotes the standard deviation of blank measures, and k represents a numerical factor chosen according to the desired confidence level. The limit of quantification is the lowest concentration that can be measured using the given analytical procedure. Both the limit of detection and the limit of quantification are constant values for the given experimental arrangement, depending on the arbitrarily chosen numerical factor k. Following IUPAC recommendation [13], the limit of detection corresponds to 3σ ($k = 3$) whilst the limit

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CHAPTER III

INFRARED SPECTROSCOPY OF XCN^+

High resolution tunable diode-laser infrared absorption spectroscopy and Fourier transform infrared absorption spectroscopy of the free radicals and molecular ions at discharge conditions.

13. Introduction to Chapter III

Molecular ions, with regard to their occurrence, are an important object of research in the fields of chemistry, physics, and astronomy. From the available information, it is known that several spectroscopic studies of the molecular ions and the reaction of ions with molecules have been carried out. Following these previous studies and aiming to expand them, this project deals with the study of the ions of CN radicals, radical cations XCN^+ (X = Br, I, Cl). Tunable infrared spectroscopy has proven to be an effective and sensitive method of detection of free radicals and molecular ions. The first study of the basic band $BrCN^+$ in IR was carried out with its use, but not the corresponding studies for ICN^+ and $ClCN^+$. Obtaining infrared spectra of the studied ions would be a great help for subsequent unique measurements in the area of microwave spectroscopy.

In this study the tunable diode laser (TDL) absorption infrared spectroscopic method has been applied for the open study of radical cation ICN^+ in the region about 2080 cm^{-1}, which is corresponding to middle of the band according to the previous studies. This experiment has been supplemented by the high resolution Fourier transform infrared (FTIR) spectroscopy. Since the TDL infrared spectroscopy provides sensitivity and the FTIR spectroscopy provides broad spectral range, these methods have been selected for investigation of combustion and burning processes including production of reactive intermediates and terminal products. The both of these explorations have been performed in the discharge plasma to simulate an exothermic medium. Our experimental arrangement is described later on.

14. Motivation and previous studies

Molecular ions and especially cations are important species on Earth and in space, in the environments such as flame, plasma, comets, the atmosphere of planets, interstellar space etc. [23]. This is the reason why molecular ions attract the attention of chemists, physicists and astronomers. Many spectroscopic studies of the molecular ions and the reaction of ions with molecules have been carried out [24].

Tunable infrared spectroscopy has proven to be an effective and sensitive method of detection of free radicals and molecular ions. The detection of small concentrations and weak absorption during spectroscopic studies of molecular ions requires the use of the methods of phase-sensitive detection of the type of speed modulation and especially production modulation [25]. It is the production modulation in hollow cathode discharges that has proven to be very promising in the spectroscopic research of the radicals and ions containing carbon and nitrogen [26]. Therefore, the production of radical cations XCN^+ (X=Cl, Br, I) in a hollow-cathode discharge with the XCN precursor and Penning ionization using atoms of helium was designed for this study. Spectroscopic constants of the mentioned radical ions are either known only partially or unknown; therefore, the spectroscopic search for rotational-vibrational transitions of these ions was included in the study. Spectroscopy in neon matrices has provided optical absorption spectra of gradients B $2\Pi 3/2 \leftarrow$ X $2\Pi 3/2$ of the cations XCN^+, transitions A $2\Sigma^+ \leftarrow$ X'$2\Pi 3/2$ of the cations ICN^+, absorption bands of CN· radical in the spectra $ClCN^+$ and $BrCN^+$ and infrared spectra of the cations ICN^+. The electronic spectra of radical cations XCN^+ has been studied using the emission spectroscopy with excitation in the gas phase by electron bombardment. Using the emission spectroscopy of supersonically

cooled XCN^+ the transitions corresponding to vibrational structures have been gradually assigned. The first study of the basic band $BrCN^+$ using the IR laser-diode spectroscopy was carried out, but not the corresponding studies for ICN^+ and $ClCN^+$. The vibrational frequency of XCN^+ in basic electronic states, and also in some excited states have been predicted using the studies based on electron spectroscopy [27]. This data is a very high-quality prediction for search in the infrared region. For this study, the investigations of the infrared region were proposed to be carried out using the sensitive laser-diode spectroscopy with possible use for millimeter and submillimeter spectroscopy.

This study about the radical cation ICN^+ is a follow-up to a previous research into the molecule $BrCN^+$ [28]. Bromocyanide radical ion (cation $BrCN^+$), which falls into the group of molecules with 15 valence electrons has been experimentally studied in the past (given the objectives of the project to produce, measure and identify the lines of ion radicals, the overview is focused only on experimental studies). The beginning of the study of this molecule dates back to the year 1955 [8]. Due to the low concentrations, and thus small intensities of the absorption lines, the first results of the detection of this ion were unusable for a more detailed characterization, as well as for the calibration accuracy we are seeking. This, however, was an important piece of knowledge for further studies, in which it has proven necessary to use the techniques like phase-sensitive detection. This technique has been also used to observed first high-quality emission spectral lines of $BrCN^+$ in 1976 [29]. In further spectral measurements that used this technique the spectral transitions $A2\Sigma^+ \rightarrow \tilde{X}2\Pi$ and $B\ 2\Sigma \rightarrow \tilde{X}2\Pi$ were identified using photoelectron spectroscopy [30]. To minimize creation of by-products, in both cases a commercial substance of relatively high purity, the radical cation $BrCN^+$ (Sigma-Aldrich, purity 98%) was used as a precursor. Three low-

resolution electron belts of the cation radical $BrCN^+$ were measured with spectroscopy using a matrix of the carrier gas neon [31]. The first vibrational spectra of two transitions have been identified in 1985 using emission spectroscopy using supersonic cooling to minimize the intensity of by-products [32]. The result of this valuable study was determination of vibrational frequencies of $BrCN^+$ in the Ω = 3/2 component X̃2Π (the basic electronic state) and several excited states. Also for the first time the value of the constant spin-orbit interaction of the unpaired electron with other electrons in the molecule was determined at 1477 cm^{-1}. This was followed by the first rotationally resolved study of this ion using the technique of laser excitation [33] and the results of the measurements for the first time determined the approximate structural parameters of the radical ion. Infrared spectroscopy with diode laser as a source of radiation for obtaining precise data from the medium infrared region was not applied until 1993 [28]. The study yielded very valuable results that can be qualitatively considered an objective of this research and that can be used with minimum error for calibration of the experiment we conducted, which is very similar in its structure to the one referred to in the mentioned study.

The result of the research is the appropriateness of use of the commercial precursor for the production of the radical ion in a quantity sufficient for the medium infrared region of the electromagnetic radiation using the technique of phase-sensitive detection and the comparison of measurements with the results of the last-mentioned study.

15. Theoretical background

Spectral characterization of radical ions containing in the molecule fluorine, chlorine, iodine or bromine is a very hard task from the spectroscopic point of view. There are several reasons for this, the most important of which is the problem of the production of these ions in a quantity sufficient for spectroscopic detection, and when this task is successfully handled, the next obstacle is their unambiguous spectral identification. The latter disadvantage can be considered as positive in a microwave area, since the molecule of the ion radical, just as the radical molecule, contains an unpaired electron, and the so-called Zeeman effect can be applied for spectral identification of individual resolved lines. In the infrared region, however, the resolution is millions of times smaller, and although the Zeeman effect would not be physically influenced, it can have no or only minimal impact in the observed spectra, which is determined by the method of detection, namely by using the higher time constants. It is therefore interesting and also necessary for further study to choose the right experimental strategy, in which an important role is played by previous studies of these species in other spectral regions (if any were published). Studying the ion radical $BrCN^+$ seemed the most promising for several reasons. The first of them is that the radical cation $BrCN^+$ in comparison with other ion radicals of the XCN^+ type is relatively well-studied molecule (not in the infrared area!), which has been described by many experimental and theoretical (ab initio calculations) studies. This leads to the second reason, which is relatively accurate knowledge of the spectral bands that have been studied, even in the spectral region selected by us, which offers a unique opportunity to use its measured lines for calibration of our spectrometer by comparing the measured lines with the lines obtained before with the minimum comparison

deviation, and then determine the relative intensity of the lines with the same wavelength, thus the sensitivity of our spectrometer against the one of the spectrometer used in previous studies. The research proved the appropriateness of use of the commercial precursor for the production of the radical ion in a quantity sufficient for the medium infrared region of the electromagnetic radiation using the technique of phase-sensitive detection and the comparison of measurements with the results of the last-mentioned study of $BrCN^+$. This examination, however, was not completely successful because of the low performance of the radiation source, and thus the instability of the whole system in the required area. The next step was to focus on the study of another representative of a series of XCN^+ molecules, namely the radical cation ICN^+ in the area around 2080 cm^{-1}, which corresponds to the center of the band, and where both the performance of the diode and the optimization of the measuring equipment were satisfactory. This time we used as a precursor the ICN with the expected vapor pressure of 0.75 Torr [34] and we registered a number of new lines emerging while using this sample, which have not, however, yet been clearly identified. This study is still ongoing and we are planning to proceed by measuring the very CN radical, which plays the key role in all studies of this nature.

16. Experimental background

Laser spectroscopic techniques are very effective tools for research of free radicals and molecular ions. Laser-diode spectroscopy, as the method used in this study, has besides its characteristic properties also many experimental differences from the rest types of molecular spectroscopies. The selectivity and sensitivity of the detection has been upgraded by involving lasers to molecular spectroscopy that made possible to measure species such as molecular cations and anions. Before the beginning whichever high resolution infrared spectroscopy experimental work is necessary to carry out the arrangement of experimental apparatus and its following optimization.

The diode-laser spectrometer has been used in the J. Heyrovsky Institute of Physical Chemistry of ASCR. This spectrometer operates in the middle infrared spectral region of electromagnetic radiation. As a source of infrared radiation is there exploited commercially available current tunable PbTeSn diode. The photons in wavenumbers range of 1832 - 2100 cm^{-1} (mid-infrared spectral area of electromagnetic radiation) are generated by electric current application to P/N transition of active layer of the diode used. Diode laser situated in a cold head of a He-cryostat is temperature stabilized by a cryogenic module, current controlled by a laser control module and frequency modulated by a modulation module. This modulated radiation is focused by a lens and led either to a Ge etalon (used to determine a relative scale for wavenumber of radiation and to visual representation of laser modes) or is led to the monochromator and to a reference and absorption cells. The monochromator of radiation with diffraction grating is used as a dispersion element for separation of laser modes. The radiation outgoing of monochromator is divided by a beam splitter – the first beam is led to the cell with reference gas

(OCS in our case) and the second beam is led to a multireflection absorption cell (water-cooled discharge cell) with a studied unstable molecular systems in the gas phase. The radiation went through an absorption cell with a sample it is thereafter focused to the InSb detector operating at a liquid nitrogen temperature. The signal from the detector is then demodulated by phase-sensitive amplifier and transferred by AD convector to the computer. As a precursor for production radical cation ICN^+ the powder of ICN and liquid of CH_3CN, and as a stable reference system the gas of OCS has been used [35].

The broad spectral range has been acquired by the Fourier transform Bruker IFS 125 HR spectrometer. This spectrometer is able to measure both the absorption and emission spectra with resolution up to 0.002 cm^{-1}. The fundamental part of the device is Michelson interferometer with the 2.5 m long tunnel of moving mirror. Inside the interferometer it occurs to the interference of polychromatic radiation emitted from the selected source of radiation. This radiation passes through the multireflection cell with the optic path 30 m and then it impinges to the detector. The spectrometer operates in the region from far-infrared radiation up to the UV area in dependence on the used beam splitter, source of radiation and detector. The nitrogen cooled InSb detector together with the CaF_2 beam splitter and tungsten source of radiation have been used in this study. The commercially provided OPUS 5.0 software has been used for the estimation of absorption intensities as well as for the comparison of rotation-vibration bands with our spectral database [36].

17. Results and discussion

Although we have expected the ICN^+ production according to the Penning ionization effect in the helium hollow cathode discharge and incidence of this ion in the region around 2082 cm^{-1} corresponding to the ν_1 vibrational mode (C-N stretch), we have acquired the set of new lines with periodic wavenumber distances. This spectrum has been recorded with the use of ICN as a sample by means of diode-laser infrared spectroscopy, and obtained lines have been verified as reaction products of this molecule in the hollow cathode discharge with helium, i.e. the lines are not visible without the precursor or without the discharge. The calibration of the obtained lines has been done with aid of well known published lines of the reference gas OCS **Figure 17-1**.

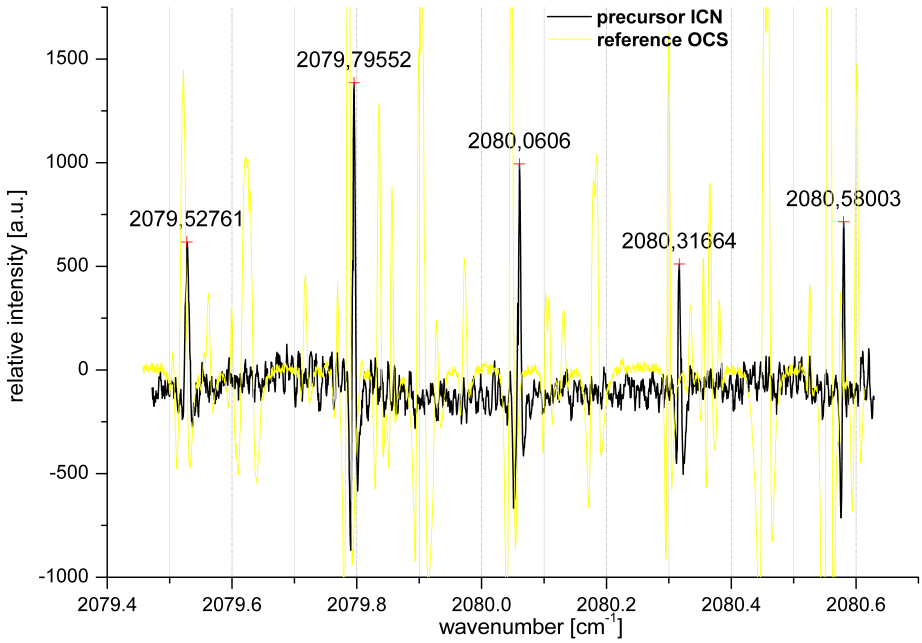

Figure 17-1: *The illustration of the lines measured by means of diode-laser spectroscopy with the precursor of ICN in discharge plasma conditions and stable reference system of OCS.*

To easily identify the unknown species, we start up experiment using the Fourier transform infrared spectroscopy to get broad spectral range going on the exothermic conditions. We have expected detection of the lines obtained by diode-laser spectroscopy in the FTIR spectra. However, in spite of the much broader spectral range which the Fourier transform spectroscopy provides, this method is not as sensitive as diode-laser spectroscopy and for that reason we could not see our previously obtained lines using the TDL.

The infrared absorption spectrum of pure ICN molecule and as well the ICN at microwave discharge has been investigated by means of Fourier transform spectroscopy (**Figure 17-2** and **Figure 17-3**). The two different spectra have been obtained and the fundamental ν_3 band corresponding to the C-N stretch with middle of the band at 2179 cm^{-1} [37] has been identified in our study (**Figure 17-2**). The absence of this band in the spectra of ICN measured in microwave discharge demonstrates evident changes in the chemical processes at exothermic conditions (**Figure 17-3**). Furthermore, the HCN and HNCO (isocyanid acid) spectrum has been identified as a product of ICN (**Figure 17-2**) and ICN with helium discharge (**Figure 17-3**). The helium discharge spectrum without the studied sample has been also added to this paper to gain compact imagination (**Figure 17-4**). In addition of usual impurities of CO2 and H2O, the FTIR spectra also showed the presence of the impurities of CO and surprisingly also HF. In the pure helium discharge the NO and N2O have been detected (**Figure 17-4**). These compounds could be present due to the possible leaks in the experimental system.

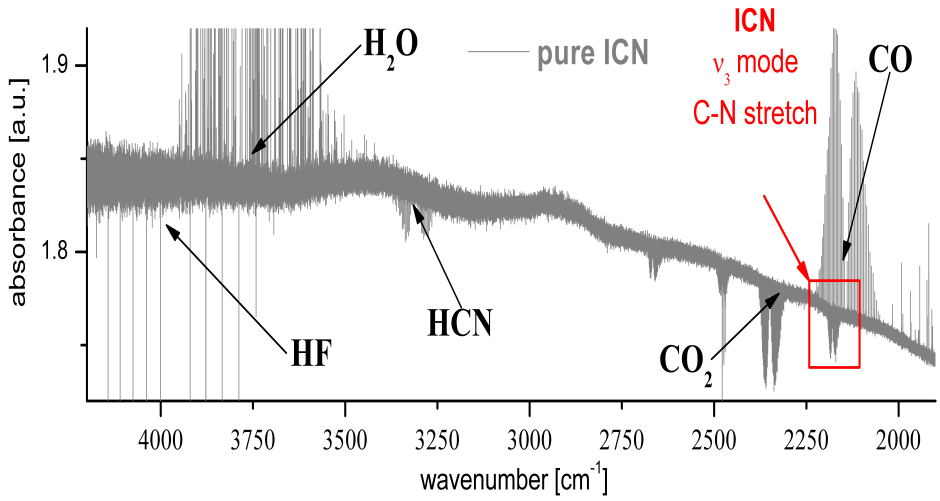

Figure 17-2: *The infrared absorption spectrum of ICN discharge gaseous products (ICN vapor pressure of 0.75 Torr at room temperature. The broad spectral range is acquired by means of Fourier transform infrared (FTIR) spectroscopy.*

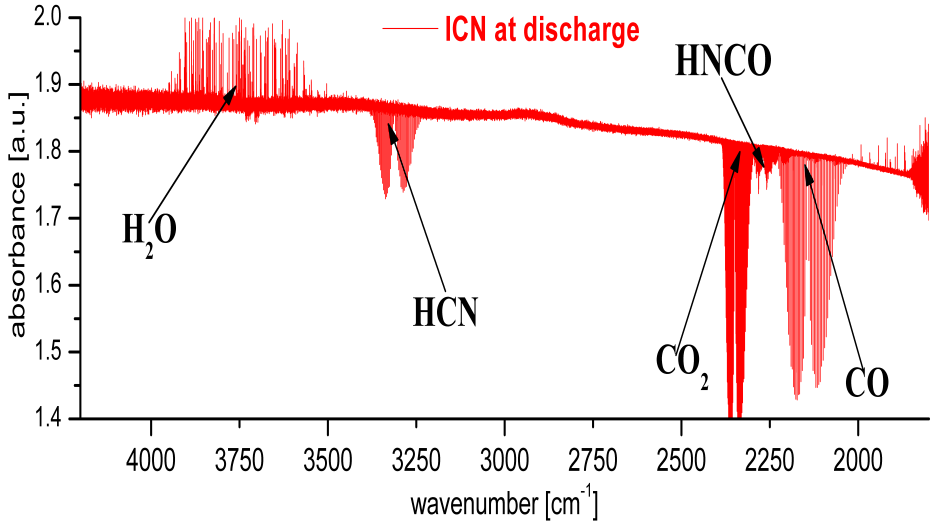

Figure 17-3: *The infrared absorption spectrum of ICN in the microwave discharge with helium. The broad spectral range has been acquired by means of Fourier transform infrared (FTIR) spectroscopy.*

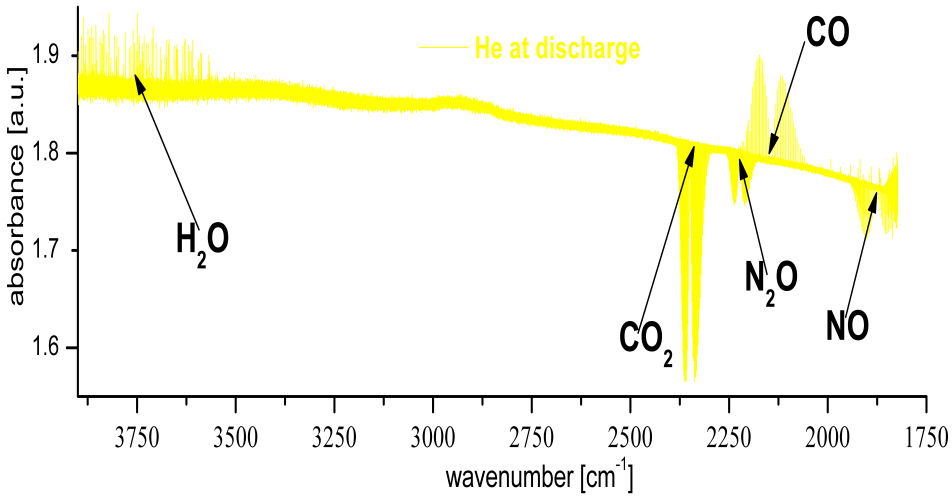

Figure 17-4: *The infrared absorption spectrum of helium microwave discharge. The broad spectral range has been acquired by means of Fourier transform infrared (FTIR) spectroscopy.*

The two separate experiments have been performed to study combustion processes (simulated exothermic medium) in hollow cathode and microwave discharge conditions. The tunable diode-laser spectroscopy has been used primarily to investigate the radical cation ICN^+ and set of the unknowns lines have been obtained. These lines indicate new species generated by hollow cathode helium discharge with sample of ICN that has been proved by Loomis Wood analyzing software. In addition of impurity of one stronger line at the position 2081.99 cm^{-1} belongs to the CO molecule, the CN• radical has been as well produces in the discharge with the use of ICN and CH_3CN as a precursor (this radical plays key role in the studies of such character). Eventually, the high-resolution Fourier transform infrared (FTIR) spectroscopy has been used to get broad spectral range and individual bands have been identified, especially the fundamental ν_3 band of main isotopic specie of $^{127}I^{12}C^{14}N$ molecule that has been proved by published article [37].

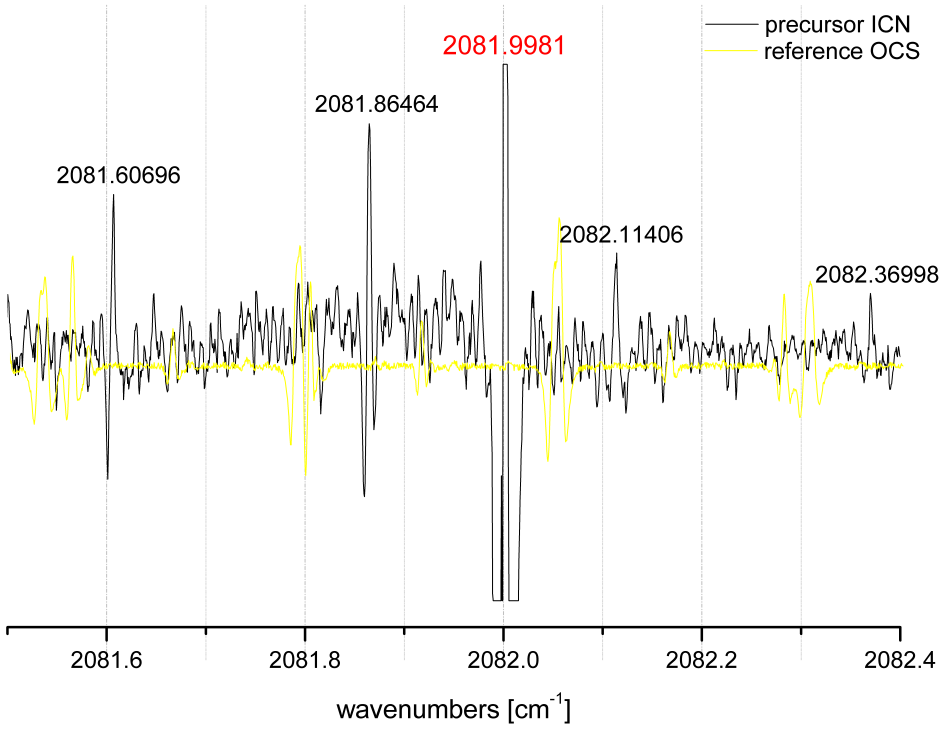

Figure 17-5: *The illustration of the much stronger saturated CO line identification as common impurity from the TDL experiment.*

18. Conclusions

The aim of this work is to describe basic principles of the selected spectroscopic methods and to outline their utilization in the field of molecular research in connection to the combustion processes and intermediates of combustion with impact on the environment. The hazardous chemical species in the gas, vapor or aerosol phases constitute serious threat for potentially exposed persons or for living environment. In the case of their abundance in the atmosphere and together with the various adverse factors interactions, these species could cause the extensive losses. With the aid of spectroscopic techniques it is possible to effectively monitor an occurrence of the individual compound or to determine concentrations of partial components in the gas mixture. The spectroscopic methods for detection of the gas phase substances provide rank of valuable information regarding concentration of hazardous chemical compounds in real time and also their spatial propagation. In general, spectroscopic methods are suitable and constantly developing techniques for detection and monitoring of many dangerous molecules, even very low concentration, important from environmental point of view (e.g. the ability to reveal contingency event at the beginning).

This thesis treated study about formadelhyde as a stable molecule representative, than study about n-penthylacetate as a model molecule of Sarin and other similar heavy molecules, and latest about molecular ions from CN radicals family.

Completely new rotational spectrum of H_2CO in the 2^1, 3^1, 4^1 and 6^1 vibrational excited states was investigated in Lille where the measurements were performed in the millimeter and submillimeter region 150 GHz - 660 GHz. One of the aims of this particular study is a more complete description of the microwave spectrum in the excited vibrational states for possible

astrophysical applications. The Cologne database involves only rotational spectrum within ground vibrational state for various isotopic species of formaldehyde and this study will contribute to this database by new lists of rotational lines in the excited states ν_4, ν_6, ν_3 and ν_2 in the millimeter-wave and submillimeter-wave region. These results have been published in Canadian Journal of Physics.

Spectrum of gaseous n-penthylacetate from FT IR spectrometer with the absorption maximum round about 1240 cm^{-1} (corresponding to the C-O stretch) has been recorded. From this broad and much weaker absosorption band of n-pentylacetate, that is available for PAS detection (9-11 μm) were distinguished three the most intense CO_2-laser emission lines and those are applicable to reach the detection limit in the order of units of ppm. Such a concentrations are expected in wind tunnel dispersion experiments. These results have been published in Journal of Molecular Spectroscopy. The models for nerve agents, as tools of simulation, are very important for risk estimation and for security and safety research.

And last but not least, the set of the lines measured by means of diode-laser spectroscopy with the precursor of ICN in discharge plasma conditions (together with stable reference system of OCS) have been observed. However, the rotational constat of this set is smaller than expecting in case of ICN^+ cation. The infrared absorption spectrum of ICN gaseous products (the broad spectral range) has been acquired by means of Fourier transform infrared (FTIR) spectroscopy (ICN vapor pressure of 0.75 Torr at room temperature) and the C-N stretch band has been identified according to the recent publication.

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